

**Theorie der Phasenübergänge
in einem eindimensionalen Gitter
mit Spin-Gitter- und
Elektron-Gitter-Kopplung**

**Inaugural-Dissertation
zur Erlangung der Doktorwürde
des Fachbereichs Physik
der Freien Universität Berlin**

vorgelegt von
Karol A. Penson
aus Warschau

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THEORY OF PHASE TRANSITIONS
ON A ONE-DIMENSIONAL LATTICE
COUPLED TO SPIN AND ELECTRON SYSTEMS

Thesis submitted for the Degree

DOCTOR RERUM NATURALIUM

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by

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I. INTRODUCTION

One dimensional (1-d) systems always attracted a considerable attention. Quasi 1-d systems consist of crystals with the atoms arranged in a set of linear chains with only weak coupling between the chains. In particular, the recently synthesised organic charge transfer salts approximate well 1-d systems having highly anisotropic quasi 1-d electronic properties (1,2,3).

Large number of quasi 1-d insulating magnets were also discovered and they turned out to be particularly susceptible to experimental investigations (4). A typical representative of highly conducting organic salts is tetrathiofulvalinium-tetracyanoquidimethan (1,2), called (TTF-TCNQ), whereas the antiferromagnet $(\text{CD}_3)_4\text{NMnCl}_3$ (called TMMC) is almost an exact physical realization of the 1-d classical Heisenberg magnet (5).

Right after the discovery of the unusual conductivity properties of TTF-TCNQ, it has been conjunctured that this compound undergoes a structural phase transition with an increase of the unit cell (6), as illustrated in Fig.1. Such a cooperative lattice distortion is expected for quasi 1-d systems. A theory for such a transition was initiated independently by Fröhlich (7) and Peierls (8) some twenty years ago. The basic physical idea behind this theory is illustrated in Fig. 2 and is the following: Consider a

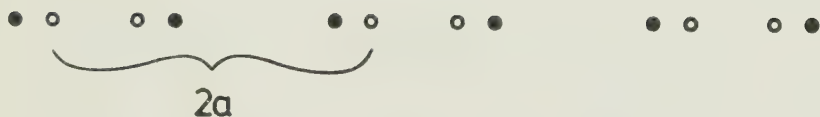
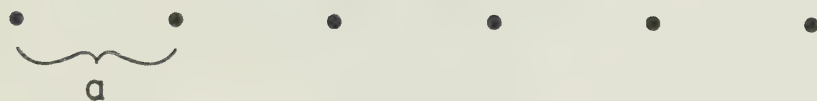


Fig. 1: A uniform chain with the period a and a distorted chain with a period $2a$.

1-d electronic system with a half filled conduction band. Then by changing the periodicity of the system ($a \rightarrow 2a$) by a cooperative lattice distortion a band gap opens up and this lowers the electronic energy. (This mechanism still occurs if the band is not half-filled). For example, consider a 1-d system of non-interacting conduction electrons, which are coupled to the lattice vibrations of a linear chain of ions. Then the electron-ion interaction can cause a temperature-dependent attractive interaction between the ions which leads to a displacement of the ions. It is easy to show mathematically by using the mean-field theory for the lattice variables, that a critical temperature T_p can always be found below which the linear lattice will develop a permanent periodic lattice distortion (8,9). This new lattice periodicity will change the energy spectrum of conduction electrons by opening up an energy gap at the Fermi energy. Such a transition will be henceforth referred to as the Peierls transition.

It is interesting to study whether other mechanisms besides the electron-ion interaction could also cause a lattice distortion in 1-d systems. For example, what happens in 1-d system of local spins? Is it possible, that the spin-lattice coupling may cause a periodic lattice distortion? This is the main problem studied in this work.

The spin-lattice interaction arises from the distance dependence of the exchange interaction $J(\vec{r}_i - \vec{r}_j)$, where $\vec{r}_i$'s

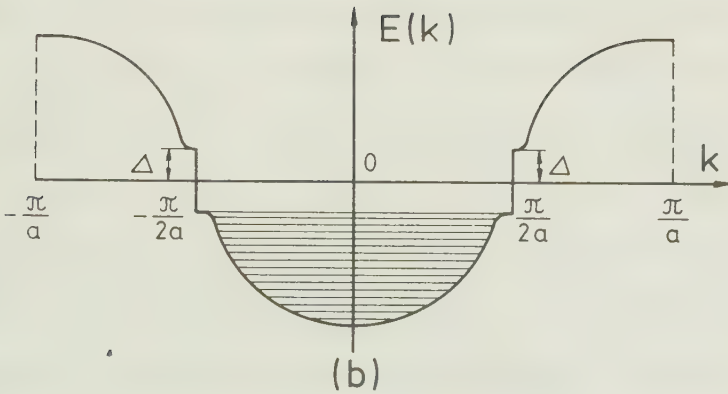
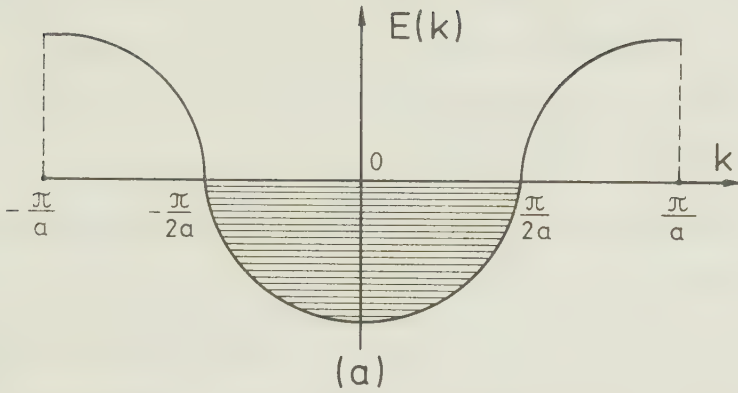


Fig. 2: a) A half-filled electronic band of a linear chain with a period a .

b) An electronic band of a distorted linear chain with an energy gap at $\frac{\pi}{2a} = K_F$

are the instantaneous positions of local spins of the ions. As in the case of the electron-lattice interaction the spin-spin interaction $J(\vec{r}_i - \vec{r}_j)$ can be expanded up to first order in the displacements $\Delta \vec{r}_{ij}$ of the ions, i.e. $J(\vec{r}_i - \vec{r}_j) = J_0(\vec{r}_{ij}^0) + J_1 \cdot \Delta \vec{r}_{ij}$, where $\vec{r}_{ij} = \vec{r}_{ij}^0 + \Delta \vec{r}_{ij}$ and where J_1 is the spin-lattice interaction.

Then, one may expect that $J_1 < \Delta r_{ij} > \vec{S}_i \cdot \vec{S}_j$ could decrease the total energy of the system as compared to the undistorted situation.

If such a periodic lattice distortion due to the spin-lattice coupling occurs, then immediately several interesting questions may be asked. For example, what is the phase diagram for the lattice phase transition and what is the role of J_0 versus the spin-lattice interaction J_1 with regard to the strength of the lattice distortion at finite temperatures and also with respect to the character of the lattice phase transition. Furthermore, how does the lattice distortion influence the spin configuration of the chain and what is the interplay of electron-lattice and spin-lattice couplings.

Concerning the first question one could speculate that the spin correlations associated with J_0 would act against the creation of a lattice distortion and lower the critical temperature at which the lattice distortion appears. Also, J_0 may affect the order of the phase transition. As far as the effect of the lattice distortion on the spin configuration is concerned one might wonder which of the various

imaginable spin configurations, see Fig. 3, could occur. By using energetical arguments one can show that some of these hypothetical configurations are excluded.

In Chapter II we present the general theory of the Peierls transition in 1-d systems consisting of electrons and classical spins. Both electrons and spins interact with a single phonon mode of the harmonic lattice. This is the same phonon mode which was responsible for the conventional Peierls transition. In our theory the lattice distortion results from the electron-lattice and spin-lattice interactions. As a model for the spin system we use the exactly soluble, isotropic 1-d n-vector model ⁽¹⁰⁾ which is a generalization of the Ising and Heisenberg models. Integrating away the electronic and spin degrees of freedom of the system one finds that the effective free energy depends only on lattice variables. Self-consistent equations for the spin- and electron-lattice coupling induced lattice distortion and its critical temperature are obtained and discussed for various values of the coupling constants. In the absence of the electron-phonon interaction it is concluded that at $T = 0$ a distorted and spin dimerized ground state (see Fig.3c,d) is obtained for $|J_0| < J_1^2 / 4\omega_0$, where the exchange constants J_0 and J_1 were defined above and where ω_0 is a characteristic lattice frequency. For $|J_0| > J_1^2 / 4\omega_0$, the ground state is undistorted. If also the presence of the electron-lattice interaction is taken into account then large J_0 values suppress the dimerized

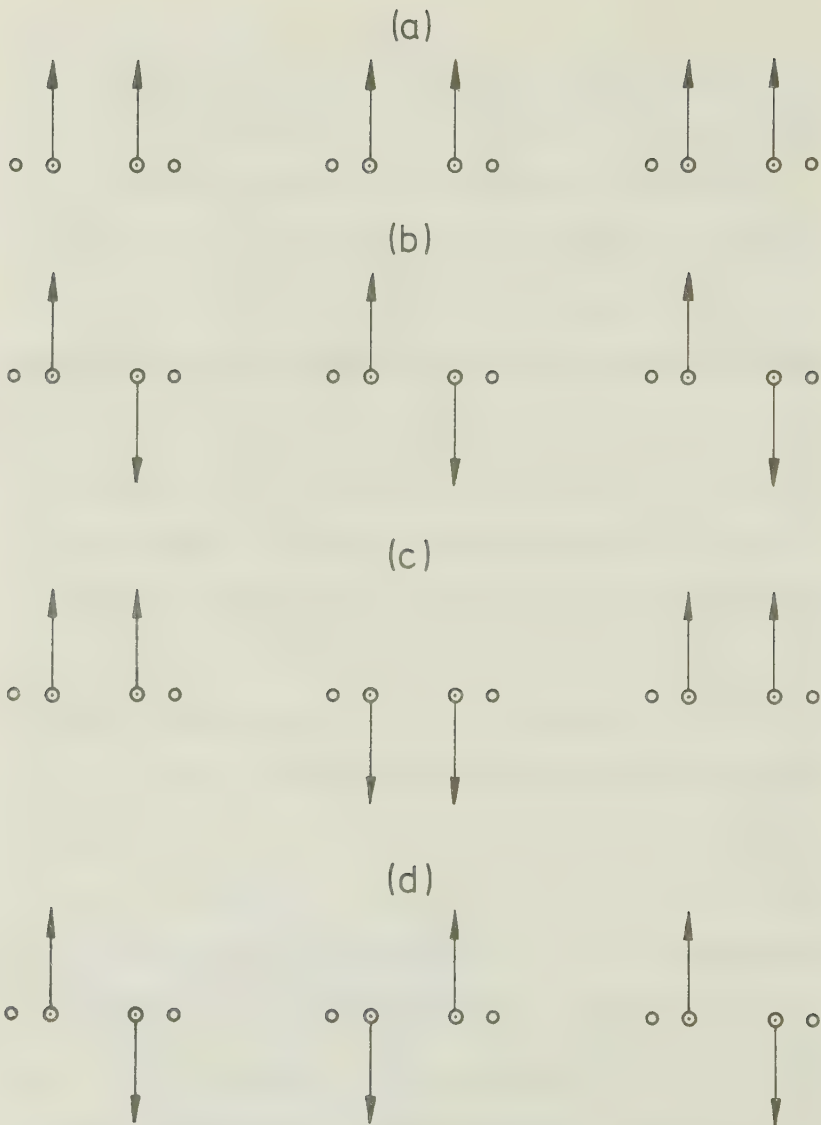


Fig. 3: Several imaginable spin configurations of the ground state of a distorted linear chain of spins.
 (c) and (d) are characteristic for classical spins,
 (b) can appear in quantum spins.

state but do not affect the lattice distortion due to the electron-lattice interaction. For the cases $n = 1$ (Ising) and $n = 3$ (Heisenberg) the Landau expansion of the free energy is performed. Similarities between the present theory and the theories of helium mixtures are found and explored. Thus complete phase diagrams with distinct regions of different critical behavior (different critical indices) of the lattice distortion $\Delta(T)$ are obtained. Finally, to learn about quantum mechanical effects, we discuss extensively the relation of our results to the Peierls lattice instability of quantum mechanical $s = 1/2$ spins within the Heisenberg model.

In Chapter III we study the Peierls lattice phase transition for the exactly soluble anisotropic X-Y spin model with spins $s = 1/2$ interacting with a single mode of the harmonic lattice. The spins are treated quantum-mechanically. The exact expression for the partition function is obtained. The temperature dependence of the lattice distortion is determined. Results for this quantum spin model are different from those found for the classical model treated in Chapter II. The lattice phase transition is only second order in quantum spin model and the ground state properties also differ from those of classical spin model. In the classical limit we recover again the results of Chapter II for the case of $n = 1$ (Ising model).

The theories described above assumed that the periodic lattice distortion arises from the spin-lattice and electron-

lattice couplings which are linear in Δr_{ij} . One knows, however, that the structure of the lattice itself can in many cases cause a structural phase transition. For example, in ferroelectrics the lattice distortion appears as a result of an interplay between nonlocal bilinear and local anharmonic terms with respect to atomic displacements. Therefore, in Chapter IV we study the possibility of a Peierls transition for an anharmonic lattice. A Hamiltonian describing a displacive ferroelectric including the electron-phonon coupling is studied in the mean field approximation. The Landau expansion of the free energy is performed. Expressions for the transition temperatures are derived. The possibility of coupled ferro- and antiferroelectric distortions is also discussed.

In Chapter II, III and IV we investigated the effect of the electron-lattice and spin-lattice interactions on the behaviour of the lattice. Similarly, one may ask what is the effect of these interactions on the critical behaviour of the spin system.

In Chapter V we analyze the effect of the spin-lattice coupling on the phase transition and critical exponents of the exactly soluble magneto-elastic model first introduced by Baker and Essam ⁽¹¹⁾. We find that the spin-lattice coupling gives rise to new "renormalized" values of magnetic critical exponents which show up only very near new transition temperature. We have also calculated as a function of pressure the temperature region near the

transition temperature where this "renormalization" sets in.

Finally, we would like to make a methodological remark: in all the calculations presented in the subsequent Chapters we have been dealing with model systems, which had at least one exactly soluble subsystem. This made it possible to perform exactly the partition sum over the variables of this exactly soluble subsystem. In other words, by "integrating away" some degrees of freedom one was then left with the effective Hamiltonian H_{eff} which did depend on a smaller number of variables. To understand it more clearly, assume for simplicity, that we are dealing with a system whose Hamiltonian is a function of two sets of degrees of freedom x_1, x_2 , $H = H\{x_1, x_2\}$. If it happens that the partition sum over the variables x_2 could be performed exactly, then it is natural to define the function $H_{\text{eff}}\{x_1\}$ by the relation

$$e^{-\beta H_{\text{eff}}\{x_1\}} = \int dx_2 e^{-\beta H\{x_1, x_2\}}, \quad \beta = (k_B T)^{-1}. \quad (I, 1)$$

$H_{\text{eff}}\{x_1\}$ has a meaning of the effective Hamiltonian associated with H after the variables $\{x_2\}$ have been "integrated away". We will be faced with similar situations considering exactly soluble magnetic systems in $d \gg 1$ coupled to elastic and electronic degrees of freedom. The idea of finding H_{eff} will be the Leitmotiv for the mathematical treatment of the physical problems studied in the following Chapters.

CHAPTER II

PEIERLS TRANSITION IN COUPLED ELECTRON AND CLASSICAL SPIN
SYSTEMS *)

*) Major portions of this Chapter have been presented during the Manchester Conference on Solid State Physics, January 1976 and have been reported in Phys. Rev. B 13, 433 (1976), and in J. Chem. Phys. (Dec. 1976).

1. INTRODUCTION

Large interest in systems of limited dimensionality has been spurred recently by synthesis and study of organic molecular crystals which at room temperatures exhibit anisotropic, quasi one-dimensional (1-d) behaviour ^(1,2,3).

Several models have been put forward to explain the various properties of 1-d systems, like the giant conductivity enhancement in tetrathioful-valene-tetracyanoquinodimethane (TTF)-(TCNQ) near 60° K ⁽⁶⁾. In particular, the theories applied the familiar Peierls argument ⁽⁸⁾ regarding the instability of 1-d metal with respect to a change in the lattice constant, as well as the soft-mode instability picture of the 1-d lattice ⁽⁹⁾.

It is the objective of the present Chapter to explore the possibilities of the systems, where in addition to electrons and phonons, also the spin variables are present. That this situation is realistic for 1-d systems is borne out by the existence of a vast number of magnetic compounds which have chain-like magnetic structures where intrachain exchange interactions are of several orders of magnitude larger than the inter-chain coupling ⁽⁴⁾. For many of these compounds the correct interpretation of experimental data can be given with the help of the exact solution of classical linear magnets. For instance, the spatial and thermal variations of spin correlations in $(\text{CH}_3)\text{NMnCl}_3$ (TMMC) can be accurately fitted with Fisher's solution ⁽¹²⁾ of the classical Heisenberg chain ⁽⁵⁾. In addition, it was established that the TMMC and related compounds

undergo a structural phase transition with the doubling of the unit cell on cooling ⁽¹³⁾, reminiscent of the Peierls transition.

Moreover, only very recently it has been unambiguously proven that 1-d magnetic chains can also display an analog of the Peierls transition ⁽¹⁴⁾. It is the spin-lattice interaction which causes this "spin-Peierls-transition" in tetrathiofulvalinium bis-cis-(1,2-perfluoromethylethylene-1,2-dithiolate)-cooper [or, TTF $\text{CuS}_4\text{C}_4(\text{CF}_3)_4$] at 12° K . At this transition the spin-lattice system dimerizes with the appearance of the lattice distortion. Another case in point is the compound TTF $\text{AuS}_4\text{C}_4(\text{CF}_3)_4$ which undergoes the spin-Peierls transition at 2.1° K ⁽¹⁴⁾. Several other materials have properties suggestive of the spin-Peierls transition: they include alkali-TCNQ salts ⁽¹⁵⁾ and chromium doped or stressed VO_2 ⁽¹⁶⁾.

As explained in the Introduction, the 1-d magnetic systems are more susceptible to the theoretical analysis as their electronic counterparts. For instance, the approximate treatment of 1-d $s = 1/2$ antiferromagnetic lattice-coupled Heisenberg chain by Pytte ⁽¹⁷⁾ can reproduce the salient features of the spin-Peierls transition ⁽¹⁴⁾.

In view of this experimental and theoretical situation we shall present here a model which studies the interplay of electron-lattice, spin-lattice and spin-spin interactions ⁽¹⁸⁾. The model consists of tightly bound electrons on a 1-d chain with electron-phonon interaction. In addition we assume on

every site a classical spin which interacts with its neighbours by means of a distance dependent exchange interaction. The general form of the Hamiltonian and the approximations used subsequently are discussed in Section 2. In Section 3 a self-consistent equation for the lattice distortion due to both electron- and spin-phonon interactions is expressed in terms of nearest-neighbours spin-spin correlation function. The essential approximation made here assumes the macroscopic occupation of only the $2k_F$ phonon mode. Section 4 discusses in detail the magnetic part of the Hamiltonian for the case of isotropic classical n-component spin model (n-vector model ⁽¹⁰⁾). Some features of the phase diagrams as the appearance of first order phase transitions, the n-dependence of the resulting critical temperatures and the magnetic ground state ($T = 0$) are presented for the limiting case of vanishing electron-phonon coupling. Section 5 presents a detailed analysis of this case for $n = 3$ (Heisenberg) model. The critical behaviour of the lattice distortion is discussed using the Landau theory of phase transitions.

Section 6 contains the presentation of the general case where all the interactions are present: we consider the dependence of the critical temperatures and the ground state properties on the various constants involved. In Section 7 a discussion of the results is given.

2. THE HAMILTONIAN OF THE SYSTEM

Consider a linear chain consisting of N ions of mass M and with spins $\vec{S}_l$ interacting with their nearest neighbours via the Heisenberg Hamiltonian. The total Hamiltonian of the system is given by

$$H = H_H + H_{el} + H_{el-latt} + H_{latt} \quad , \quad (11,1)$$

where the spin Hamiltonian H_H is given by

$$H_H = - \sum_l J_{l,l+1} \vec{S}_l \cdot \vec{S}_{l+1} \quad . \quad (11,2)$$

The longitudinal vibrations of the chain are described by the usual harmonic Hamiltonian

$$H_{latt} = \sum_l \frac{p_l^2}{2M} + \frac{1}{2} K \sum_l (u_{l+1} - u_l)^2 \quad , \quad (11,3)$$

where u_l denotes the deviation of the l -th ion from its equilibrium position R_l^0 and K is the elastic constant. The coupling constant of the Heisenberg Hamiltonian H_H is assumed to be a function of the distance between the ions. We expand now $J_{l,l+1}$ in terms of the atomic displacement and keep only the linear terms. Then

$$J_{l,l+1} \equiv J(u_l - u_{l+1}) = J_0 + J_1 \cdot (u_l - u_{l+1}), \quad J_1 \equiv \nabla J_{l,l+1} \quad (11,4)$$

The tight-binding electrons are represented in terms of Wannier electron operators $C_{l\sigma}^\dagger, C_{l\sigma}$ by

$$\begin{aligned} H_{el} + H_{el-latt} = & \sum_{l\sigma} t_{l,l+1} (C_{l\sigma}^\dagger C_{l+1\sigma} + C_{l+1\sigma}^\dagger C_{l\sigma}) + \\ & + \sum_{l\sigma} g_{l,l+1} (C_{l\sigma}^\dagger C_{l+1\sigma} + C_{l+1\sigma}^\dagger C_{l\sigma}) (u_{l+1} - u_l) \quad , \quad (11,5) \end{aligned}$$

where $t_{l,l+1}$ is the hopping integral and $g_{l,l+1}$ is the electron-phonon interaction coupling constant. Writing

$$u_l = \sum_q \frac{1}{(NM)^{1/2}} e^{iq \cdot R_l^0} Q(q)$$

and introducing the usual phonon creation and annihilation operators b_q^+ and b_q we obtain

$$H = -J_0 \sum_i \vec{S}_i \cdot \vec{S}_{i+1} - \sum_{iq} \frac{J_1}{4} (1 - e^{iqa}) e^{iqR_i} (b_q + b_{-q}^+) \vec{S}_i \cdot \vec{S}_{i+1} + \\ + \sum_{k\sigma} \epsilon(k) c_{k\sigma}^+ c_{k\sigma} + \sum_{kq\sigma} \frac{1}{2} g(k, q) c_{k\sigma}^+ c_{k+q\sigma} (b_q + b_{-q}^+) + \\ + \sum_q \omega_0(q) b_q^+ b_q \quad (\hbar = k_B = 1), \quad (11^6)$$

where $\omega_0(q) = \left(\frac{4K}{Ma^4} \right)^{1/2} \left(\sin \frac{qa}{2} \right)^2$, a is the lattice constant, $\epsilon(k) = 2t_0 \cos ka - \mu$, where μ is the chemical potential, and $g(k, q)$ is the appropriately defined electron-phonon coupling constant. The classical argument of Peierls⁽⁸⁾ implies that a regularly spaced chain structure becomes unstable with respect to a static periodic distortion of a period $2k_F = \frac{\pi}{a} \sqrt{N}$ (if $k_F < \frac{\pi}{2a}$) or $2 \cdot (\frac{\pi}{a} - k_F)$ (if $k_F > \frac{\pi}{2a}$), where k_F is the Fermi vector of electronic system and N is the number of electrons per atom. We shall limit ourselves now to the case $N = 1$ (half filled electronic band), single out from all the q -summations only the $q_0 = 2k_F$ term and assume $g(k, q_0) = g$. Using then $\exp(iqR_i) = (-1)^i$ and substituting everywhere for $b_{q_0}^+$ and b_{q_0} the lattice distortion $\Delta = \langle b_{q_0}^+ \rangle$ we obtain the effective Hamiltonian H'

$$H' = -J_0 \sum_i \vec{S}_i \cdot \vec{S}_{i+1} - \sum_i (-1)^i J_1 \Delta \vec{S}_i \cdot \vec{S}_{i+1} + \\ + \sum_{k\sigma} \epsilon(k) c_{k\sigma}^+ c_{k\sigma} + g \Delta \sum_{k\sigma} c_{k\sigma}^+ c_{k+q_0\sigma} + N \omega_0 \Delta^2 \quad (11^7)$$

where $\omega_0 = \omega_0(q_0)$.

The above Hamiltonian describes the uncoupled spin and electron systems both interacting with a single, macroscopically occupied $2k_F$ phonon mode. The spin-phonon coupling effectively causes the alternating of the part of the exchange interaction. The electron-phonon coupling produces a gap at the

Fermi surface of the electron energy spectrum. Both of these effects are described by a single order parameter Δ .

3. SELF-CONSISTENT CALCULATION OF THE TEMPERATURE DEPENDENCE OF THE LATTICE DISTORTION $\Delta(T)$

The equilibrium properties of the order parameter $\Delta(T)$ are to be determined by the minimization of the free energy corresponding to the Hamiltonian H' . The electronic part of H' can be diagonalized by a Bogoliubov-Valatin type of transformation. Then the new electron energies exhibit a gap at $k = k_F$ and are given by

$$E(k) = \text{sgn}[\epsilon(k)] \sqrt{\epsilon^2(k) + (g\Delta)^2} \quad (11,8)$$

Consequently, $F_{el} + F_{ph}$ can be calculated to get

$$F_{el}(\Delta, T) + F_{ph}(\Delta, T) = -\frac{2}{\beta} \sum_{\epsilon(k) > 0} \ln \left\{ 2 \cosh \left[\frac{1}{2} \beta E(k) \right] \right\} + N \omega_0 \Delta^2, \quad (\beta = \frac{1}{T}) \quad (11,9)$$

For calculating the magnetic part F_M of the free energy we use the fact that the partition function of 1-d classical magnetic system is always a product of bonds, $Z_M = \prod_{i=1}^{N-1} z_i$. Since we have $N/2$ bonds $J_0 + J_1 \Delta$ and $N/2$ bonds $J_0 - J_1 \Delta$ and assuming N large, the magnetic part of the free energy reads

$$\begin{aligned} F_M(\Delta, T) &= -\frac{1}{\beta} \ln Z_M = \\ &= -\frac{N}{2\beta} \left\{ \ln z(\beta(J_0 + J_1 \Delta)) + \ln z(\beta(J_0 - J_1 \Delta)) \right\}. \quad (11,10) \end{aligned}$$

We now replace the k summation in Eq.(11,9) by the integration over the density of states $N(\epsilon)$. Furthermore, we use the general formula for the n.n. spin-spin correlation function

$$\langle \vec{S}_i \cdot \vec{S}_{i+1} \rangle = - \frac{\partial F_M[\{J_{L,L+1}\}]}{\partial J_{L,L+1}}.$$

Then, from $\frac{\partial F}{\partial \Delta} = 0$, $F = F_{el} + F_{ph} + F_M$, one finds

$$\begin{aligned} \frac{J_1}{4\omega_0} \left\{ \langle \vec{S}_i \vec{S}_{i+1} (\beta(J_0 + J_1 \Delta)) \rangle - \langle \vec{S}_i \vec{S}_{i+1} (\beta(J_0 - J_1 \Delta)) \rangle \right\} + \\ + \Delta \frac{g^2}{2\omega_0} \int_0^{\epsilon_F} d\epsilon N(\epsilon) \frac{\tanh \frac{\beta}{2} \sqrt{\epsilon^2 + (g\Delta)^2}}{\sqrt{\epsilon^2 + (g\Delta)^2}} = \Delta, \end{aligned} \quad (11,11)$$

where ϵ_F is the Fermi energy and $N(\epsilon)$ is the electronic density of states per atom. Eq.(11) gives $\Delta = \Delta(T)$. We see that the behaviour of the gap in the electronic spectrum is determined self-consistently by the nearest neighbour spin-spin correlation functions. For the case

$J_1 = 0$ Eq.(11,11) reduces to the BCS-like⁽¹⁹⁾ equation for Peierls distortion from the Fröhlich Hamiltonian^(8,20).

To study the behaviour of Eq.(11,11) near the transition temperature T_c for a second order transition we expand it for small Δ .

Then, from $\Delta = 0$ the following expression for the transition temperature T_c

$$\begin{aligned} \frac{J_1}{4\omega_0} \frac{\partial}{\partial \Delta} \left\{ \langle \vec{S}_i \vec{S}_{i+1} (\beta(J_0 + J_1 \Delta)) \rangle - \langle \vec{S}_i \vec{S}_{i+1} (\beta(J_0 - J_1 \Delta)) \rangle \right\} \Big|_{\Delta=0} + \\ + \frac{g^2}{2\omega_0} \int_0^{\epsilon_F} \frac{d\epsilon}{\epsilon} N(\epsilon) \tanh \frac{\beta_c \epsilon}{2} = 1 \end{aligned}$$

is obtained.

The exact evaluation of the magnetic free energy F_M is possible only for a narrow class of magnetic model systems. We shall turn now to one of them, the physically appealing classical n -vector model of Stanley⁽¹⁰⁾ which will allow in some cases more detailed examination of Eqs. (11,11) and (11,12).

4. APPLICATION OF THE THEORY TO THE n -VECTOR MODEL SPIN SYSTEM

If our magnetic system is assumed to be described by the isotropic, classical, n -component spins interacting via Heisenberg Hamiltonian H_H given by Eq. (2), then all its properties can be extracted from the exact solution of Stanley⁽¹⁰⁾. In particular, the partition function of the magnetic part of the Hamiltonian (7) is given by

$$Z_M^{(n)}(\Delta, T) = (1 + \delta_{1,n}) \Gamma^N\left(\frac{n}{2}\right) \times \\ \times \left[\frac{\beta}{2} (\mathbf{J}_0 + \mathbf{J}_1 \Delta) \right]^{\frac{N}{2} (1 - \frac{n}{2})} \cdot \left[\frac{\beta}{2} (\mathbf{J}_0 + \mathbf{J}_1 \Delta) \right]^{\frac{N}{2}} \cdot \left[\frac{\beta}{2} (\mathbf{J}_0 - \mathbf{J}_1 \Delta) \right]^{\frac{N}{2} (1 - \frac{n}{2})} \cdot \left[\frac{\beta}{2} (\mathbf{J}_0 - \mathbf{J}_1 \Delta) \right]^{\frac{N}{2}} \quad (11,13)$$

where $\Gamma(z)$ denotes the gamma function and $I_n(z)$ is the modified Bessel function of the first kind of the order n . The magnetic free energy F_M can then be written up to an additive constant as

$$F_M(\Delta, T) = -\frac{N}{2\beta} (1 - \frac{n}{2}) \left\{ \ln \left(\frac{\beta}{2} (\mathbf{J}_0 + \mathbf{J}_1 \Delta) \right) + \ln \left(\frac{\beta}{2} (\mathbf{J}_0 - \mathbf{J}_1 \Delta) \right) \right\} + \\ -\frac{N}{2\beta} \left\{ \ln I_{\frac{n}{2}-1} \left(\beta (\mathbf{J}_0 + \mathbf{J}_1 \Delta) \right) + \ln I_{\frac{n}{2}-1} \left(\beta (\mathbf{J}_0 - \mathbf{J}_1 \Delta) \right) \right\}. \quad (11,14)$$

(More details about the partition function of the n -vector model can be found in the Appendix A). Using now the property of derivatives of modified Bessel functions

$$I_n'(z) = I_{n+1}(z) \pm \frac{n}{z} I_n(z) \quad (11,15)$$

the Eq. (11,11) can be rewritten as

$$\frac{J_1}{4\omega_0} \left\{ \frac{I_{\frac{n}{2}}(\beta(J_0 + J_1\Delta))}{I_{\frac{n}{2}-1}(\beta(J_0 + J_1\Delta))} - \frac{I_{\frac{n}{2}}(\beta(J_0 - J_1\Delta))}{I_{\frac{n}{2}-1}(\beta(J_0 - J_1\Delta))} \right\} + \Delta \frac{g^2}{2\omega_0} \int_0^{\epsilon_F} d\epsilon N(\epsilon) \frac{\tanh \frac{\beta}{2} \sqrt{\epsilon^2 + (g\Delta)^2}}{\sqrt{\epsilon^2 + (g\Delta)^2}} = \Delta, \quad (11.16)$$

and the eq.(11.12) takes on the form

$$\frac{\beta_c J_1^2}{2\omega_0} \left\{ 1 + \frac{(1-n)}{\beta_c J_0} \frac{I_{\frac{n}{2}}(\beta_c J_0)}{I_{\frac{n}{2}-1}(\beta_c J_0)} - \frac{I_{\frac{n}{2}}^2(\beta_c J_0)}{I_{\frac{n}{2}-1}^2(\beta_c J_0)} \right\} + \frac{g^2}{2\omega_0} \int_0^{\epsilon_F} \frac{d\epsilon N(\epsilon)}{\epsilon} \tanh \frac{\beta_c \epsilon}{2} = 1 \quad (11.17)$$

where $I_{\frac{1}{2}}(z)/I_{-\frac{1}{2}}(z) = \tanh(z)$ and $I_{\frac{3}{2}}(z)/I_{\frac{1}{2}}(z) = \coth(z) - \frac{1}{z} = \mathcal{L}(z)$ (Langevin function).

We observe that for $J_1 = 0$

$$g \Delta(T=0) = g \Delta_0^P = 2\epsilon_F \exp\left(-\frac{1}{\frac{g^2 N(0)}{2\omega_0}}\right) \quad (11.18a)$$

and

$$T_c^P = 1.14 \epsilon_F \exp\left(-\frac{1}{\frac{g^2 N(0)}{2\omega_0}}\right) \quad (11.18b)$$

Furthermore, note that for $g = 0$ Eqs.(11.16) and(11.17) describe the lattice distortion $\Delta(T)$ resulting only from the spin-phonon interaction. In this case, however, due to the presence of two coupling constants J_0 and J_1 the picture of the phase transitions depends sensitively on the value of J_0 . This perhaps can be best illustrated in the case of Ising spins ($n = 1$).

Then Eq.(11.16) reads

$$\frac{J_1}{2\omega_0} \left[\frac{\sinh 2\beta J_1 \Delta}{\cosh 2\beta J_0 + \cosh 2\beta J_1 \Delta} \right] = \Delta \quad ; \quad (g=0) \quad (11.19)$$

if we denote $\Delta_0^S = J_1/2\omega_0$ then the $T \rightarrow 0$ limit of eq.(11.19), i. e.

$$\Delta_0^S (e^{2\beta(J_0 - J_1\Delta)} + 1)^{-1} \approx \Delta,$$

tells us that the necessary condition for $\Delta(T=0) \neq 0$ is $J_1 \Delta_0^S > J_0$

or

$$J_0 < \frac{J_1^2}{2\omega_0} \quad (11.20)$$

It can be shown quite generally that the inequality (11,20) remains valid for all n . For $J_0 > J_1^2/2\omega_0$ one finds that Δ is identically zero for all the temperatures.

The set of $T = 0$ solutions of Eq. 19), i. e.

$$\Delta \equiv 0 \quad \text{for} \quad J_0 > \frac{J_1^2}{2\omega_0} \quad (11,21a)$$

$$\Delta = \begin{cases} 0 \\ \Delta_0^s \end{cases} \quad \text{for} \quad J_0 < \frac{J_1^2}{2\omega_0} \quad \begin{matrix} (11,21b) \\ (11,21c) \end{matrix}$$

has to be tested for stability against small perturbations. It is easily checked that both the solutions Eqs. (11,21b) and (11,21c) are stable but (11,21c) is metastable with respect to (11,21b) in the interval

$$\frac{J_1^2}{4\omega_0} < J_0 < \frac{J_1^2}{2\omega_0} \quad (11,21d)$$

In the following paragraph the ground state properties are derived by means of a simple argument. It is shown there that the metastable state is not confined to the interval (11,21d) but to $J_0 > \frac{J_1^2}{4\omega_0}$. That this is not obtained from Eq. (11,19) is due to the fact that in the limit $T \rightarrow 0$ the system undergoes a phase transition to the long range ordered state. This implies for the Ising model that F_M has to be calculated with both eigenvalues of the transfer matrix leading to the correct result.

Irrespective of n we obtain for the ground state energies of the ferromagnetic ($F, \vec{S}_i \cdot \vec{S}_{i+1} = 1$), antiferromagnetic ($AF, \vec{S}_i \cdot \vec{S}_l = -1$) and dimerized ($D, \vec{S}_l \cdot \vec{S}_{l+1} = (-1)^l$) states the following values:

$$\frac{1}{N} E_o^{F(AF)} = \text{Min} (\bar{J}_0 + \omega_o \Delta^2) = \bar{J}_0, \quad (11,22a)$$

$$\frac{1}{N} E_o^D = \text{Min} (-J_1 \Delta + \omega_o \Delta^2) = -\frac{J_1^2}{4\omega_o}. \quad (11,22b)$$

Comparing the energies of the undistorted and dimerized ordered states, we conclude that at $T = 0$

$$|J_0| > \frac{J_1^2}{4\omega_o}, \quad \text{undistorted} \quad (11,23a)$$

$$|J_0| < \frac{J_1^2}{4\omega_o}, \quad \text{dimerized} \quad (11,23b)$$

holds. Let us point out that at $T = 0$ there is a phase transition to a spin long range ordered state for all coupling constants.

In order to check whether the inequality (11,23a) describing the condition for the appearance of a lattice distortion can be satisfied for real materials some knowledge about the functional form of $J = J(r)$ is needed. It has been emphasized that the 1-d magnets belong to very few systems which permit good experimental measurements of $J(r)$. More specifically, the assumption that the exchange varies as some inverse power of the lattice spacing $J(r) = Ar^{-n}$ was experimentally confirmed by Rogers et al. (21) who found values of n close to 11. For other, 3-d substances, as Gd, the typical values of n were estimated to be $n = 12$ (22).

With $J(r) = Ar^{-n}$ we obtain for (11,23b) with the Debye energy $\omega_D = \alpha^2 \omega_o$

$$\frac{n^2 J}{4\omega_o} > 1. \quad (11,24)$$

Even for $n = 8$ and for $J = 10^0$ K, $\omega_D = 100^0$ K, which are typical values, the condition (11,24) is satisfied.

The conditions Eqs. (123) illustrate the effect of the strong spin correlations associated with J_0 on the spin-phonon coupling induced lattice distortion. Sufficiently large J_0 will destroy the lattice distortion. The situation here is similar to the incompatibility of strong Coulomb correlations and the Peierls distortion in electron-phonon systems⁽²³⁾.

Important effects of J_0 on the picture of the phase transition are not limited to the ground state. It turns out that for finite temperatures J_0 can induce the change of the order of the phase transition: for large J_0 Eq. (119) describes the first order transition in $\Delta(T)$. This is not unexpected, since a closer examination of Eq. (119) reveals that it bears a striking resemblance to the Blume, Emery and Griffiths theory of tricritical points in ^3He - ^4He mixtures⁽²⁴⁾. Our Δ plays the rôle of the superfluid order parameter of Blume et al.⁽²⁴⁾. Without developing a full analogy here we note only that the bracketed part of the l.h.s. of Eq. (119) behaves for large Δ qualitatively similar to $\tanh(2\beta J_1 \Delta)$ allowing only for one non-zero solution (second order phase transition). If however $J_0 > T \ln 2$ the bracketed part can have an inflection point and the second derivative of the l.h.s. of (119) with respect to Δ changes sign. This signals the onset of the first order phase transition (Fig. 4). Similar results are obtained for other n . The analytic expression for the second order phase transition temperature $T_c = T_c^{(n)}(J_0, J_1, \omega_0)$ cannot be extracted in a closed form from Eq. (17) ($g = 0$). Using however the small argument expansion of the modified Bessel functions

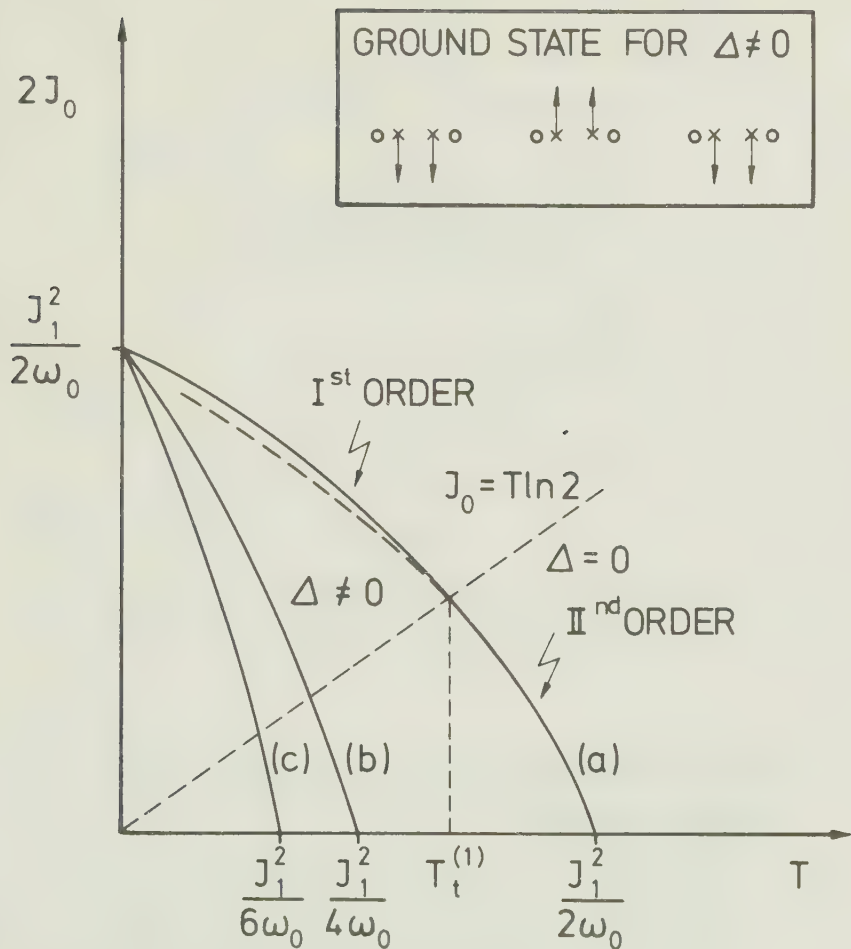


Fig. 4: Critical temperatures for the lattice distortions as a function of $2J_0$ for different n ($g=0, J_1=\text{const.}$) a) $n=1$, b) $n=2$, c) $n=3$. For $T \rightarrow 0$ all the curves coalesce for $J_0 = J_1^2 / 4\omega_0$. Below $T_t^{(1)}$ the transition is of first order. In the insert the dimerized ground state $[\vec{S}_1 \cdot \vec{S}_{1+1} = (-1)^1]$ is depicted.

$$I_n(z) \approx \frac{(2/2)^n}{\Gamma(n+1)} + \dots \quad (n \neq -1, -2, \dots)$$

we get for $T_c^{(n)}(0, J_1, \omega_0)$ the expression

$$T_c^{(n)}(0, J_1, \omega_0) = \frac{J_1^2}{2\omega_0} \left[\frac{1}{n} - O\left(\frac{J_0^2}{\omega_0^2}\right) + \dots \right]. \quad (11,25)$$

Combining Eqs. 21c) and 25) we observe that

$$\frac{J_1 \Delta_0^s}{T_c^{(n)}(0, J_1, \omega_0)} = n, \quad (11,26)$$

which is equivalent to the "universality" relation Eq.(11,18b), known also from the theory of superconductivity.⁽¹⁹⁾

Increasing J_0 , first the critical temperature for distortion is lowered, then the order of transition changes and finally the transition becomes suppressed altogether.

5. CRITICAL BEHAVIOUR OF THE LATTICE DISTORTION FOR $n = 3$ (HEISENBERG) CHAIN.

In the previous section we have pointed out the striking similarity between the temperature dependence of $\Delta(T)$ for $n = 1$ and that of the superfluid order parameter of the Blume, Griffiths and Emery ⁽²⁴⁾ theory of helium mixtures. The main feature of the phase diagram was the appearance of the cross-over between the first and second order phase transitions in $\Delta(T)$.

We shall explicitly demonstrate now that also for $n = 3$, which is the Heisenberg model (12) a similar behaviour of $\Delta(T)$ results. Note, that for $n = 3$ the free energy of the spin model is completely different from that of Blume et al. (24) The free energy for the case $n = 3$ reads (see Eq. (11,13)):

$$\begin{aligned} f^{(3)} &= F^{(3)}/N = \\ &= f_0^{(3)}(T) - \frac{1}{2\beta} \ln \frac{\sinh(\beta(J_0+J_1\Delta)) \sinh(\beta(J_0-J_1\Delta))}{\beta(J_0+J_1\Delta) \beta(J_0-J_1\Delta)} + \omega_0 \Delta^2, \end{aligned} \quad (11,27)$$

where $\beta = (k_B T)^{-1}$ and $f_0^{(3)}$ is Δ independent. We shall be interested in the behaviour of $f^{(3)}$ near the phase transition, i.e. for $\Delta(T)$ small. Therefore we expand the free energy $f^{(3)}(\Delta, T)$ in power series in the order parameter Δ retaining terms up to order Δ^6 . Then

$$\begin{aligned} f^{(3)}(\Delta, T) - f_0^{(3)} &= \\ &= \frac{1}{2!} a(T, J_0) \Delta^2 + \frac{1}{4!} b(T, J_0) \Delta^4 + \frac{1}{6!} c(T, J_0) \Delta^6 + \dots \end{aligned} \quad (11,28)$$

where $x = J_1^2/\omega_0$.

The Eq. (11,28) represents the Landau expansion of the free energy $f^{(3)}(\Delta, T)$. In order to be able to analyse the phase transition displayed by Δ the explicit knowledge of the temperature dependence of the coefficients of the Landau expansion is needed. It turns out that the coefficients a and b change their signs for certain temperatures T_c and T_0 respectively and that $c > 0$. Accordingly, we expand now a and b near T_c and T_0 and get

$$a(T, x, J_0) \cong a' \cdot (T - T_c(x, J_0)) \quad , \quad (11, 29a)$$

and

$$b(T, J_0) \cong b' \cdot (T - T_0(J_0)) \quad (11, 29b)$$

with $a' = \frac{2\omega_0}{T_c}$, $b' = 8J_1^4 k_B \beta_0^4 S(2\beta_0 J_0)$ and $S(x) =$
 $= (2 + \cosh x)(1 - \cosh x)^{-2}$. The characteristic temperatures T_c and T_0 themselves are given as solutions of

$$T_c = \frac{x}{k_B} \left[\left(1 - \cosh \frac{2J_0}{k_B T_c} \right)^{-1} + \frac{(k_B T_c)^2}{2J_0^2} \right] \quad (11, 30a)$$

and

$$T_0 = \frac{J_0}{k_B} \left[\frac{4}{3} S\left(\frac{2J_0}{k_B T_0}\right) \right]^{\frac{1}{4}} \quad (11, 30b)$$

Note, that $T_c(x, 0) = x/6k_B$, in accordance with Eq. (11, 25).

The general analysis of the Landau expansion in the form

(11, 28) indicates the possibility of the second as well as first order phase transitions (26). We have collected the

necessary information as well as the properties of $\Delta(T)$ resulting from (11, 28) in the Appendix B. Using the results

of this Appendix one sees that the free energy expansion

(11, 28) describes a second order transition in Δ whenever $a = 0$ and $b > 0$. The cross-over temperature T_t between first

and second order is given by the simultaneous solution of

$a = b = 0$. By this reasoning we obtain the phase diagram

shown in Fig. 6. For the temperatures lower than T_t the

system undergoes the first order phase transition along the surface in (T, J_0, x) space described by two conditions (26)

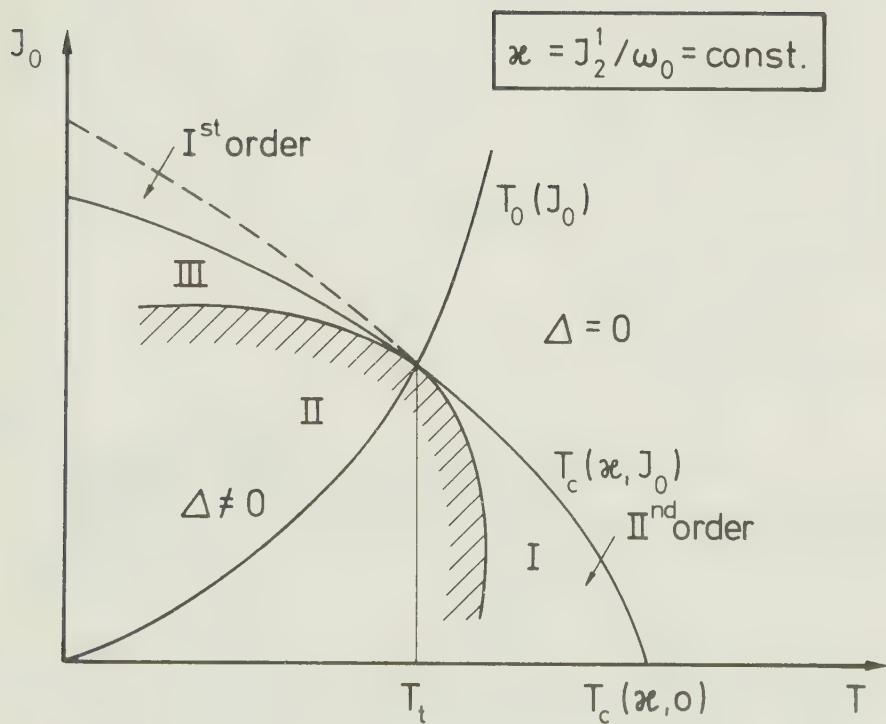


Fig. 6: The phase diagram of $\Delta(T)$ for the Heisenberg chain, indicating different regions of critical behaviour:
 I: classical, II: tricritical, III: renormalized exponents.

$$f^{(3)}(\Delta, T) = f_0^{(3)} \quad , \quad (11, 31a)$$

$$\partial f^{(3)}(\Delta, T) = 0 \quad . \quad (11, 31b)$$

We recall that along the first order transition line (for instance for $\mathcal{X} = \text{const.}$) the free energies of the distorted and undistorted phases are equal. An alternative, although totally equivalent method of analysing $\Delta(T)$ consists of solving the self-consistency equation $\partial f^{(3)}/\partial \Delta = 0$ for arbitrary Δ , using the original form of $f^{(3)}$ rather than its small Δ expansion (11, 28). We have solved numerically the self-consistency equation

$$\frac{J_1}{2\omega_0} H(\Delta) = \Delta \quad , \quad \text{where} \quad (11, 32)$$

$$H(\Delta) = \frac{\sinh 2\beta J_1 \Delta}{\cosh 2\beta J_1 \Delta - \cosh 2\beta J_0} + 2 \cdot \frac{2\beta J_1 \Delta}{(2\beta J_0)^2 - (2\beta J_1 \Delta)^2} \quad (11, 33)$$

The solution is represented graphically in Fig. 5. By increasing J_0 the curves of $H(\Delta)$ become increasingly S-shaped. They can correspondingly have two non zero intersection points with the function $\frac{2\omega_0}{J_1} \Delta$ (Eq. (11, 32)). This indicates the onset of the first order phase transition. We did not pursue this method and it was the Landau expansion which gave us the phase diagram. We can conveniently divide the phase diagram into three regions which differ by their sets of critical exponents, see Fig. 6 : Below $T_c(0, \mathcal{X})$ there is the second order transition line, across which there

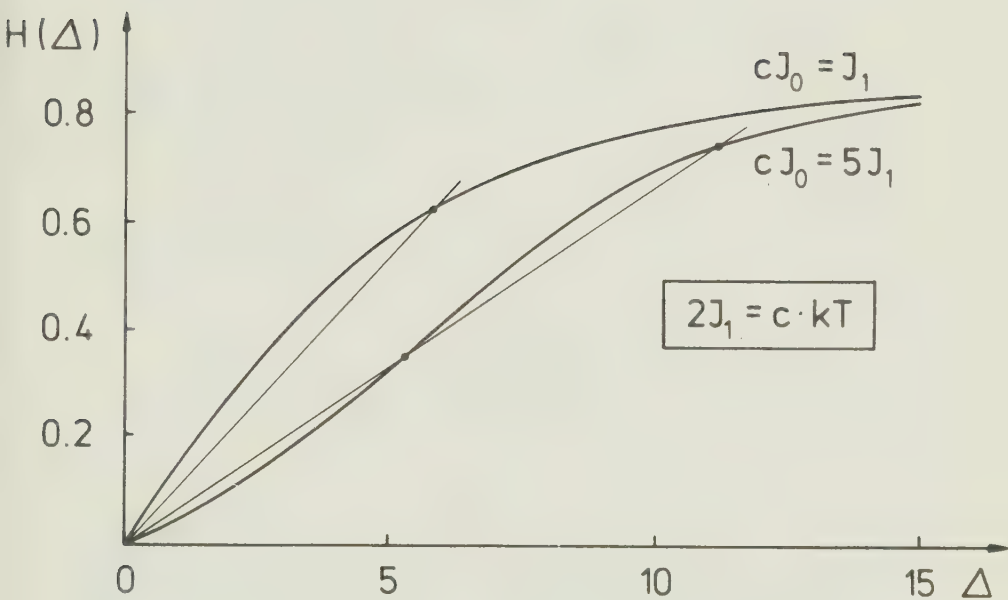


Fig. 5: The function $H(\Delta)$ (Eq. (II,33)) plotted for different values of J_0 ($c = \text{const}$). By increasing J_0 the curve becomes S - shaped indicating the onset of first order phase transition.

is the set of the "molecular field" exponents $(\alpha'_t, \beta_t, \gamma'_t, \delta_t) = (0, \frac{1}{2}, 1, 3)$ (region I). For $T_c(J_0, x) = T_t$ the second order line merges continuously into the first order line. For all the paths in the (J_0, T) plane approaching T_t the temperature dependence of the fourth order terms in (II, 28) reflects itself in the new set of so called tricritical exponents (25)

$(\alpha'_t, \beta_t, \gamma'_t, \delta_t) = (\frac{1}{2}, \frac{1}{4}, 1, 5)$. This is the region II of Fig. 6. In the region III the exponents take on so called "renormalized" values (25) $(\alpha'_r, \beta_r, \gamma'_r) = (\frac{-\alpha_t}{1-\alpha_t}, \frac{\beta_t}{1-\alpha_t}, \frac{\gamma_t}{1-\alpha_t}) = (1, \frac{1}{2}, 2)$ because the boundary of this region and the second order transition line has the same slope at $T = T_t$ (26). Another example of such renormalization of critical exponents will be considered in detail in Chapter V.

We should emphasize that our results were obtained from the expansion (II, 28) which could in turn be obtained from the exact expression for $f^{(3)}$. In this connection it is of interest that Theumann and Høye (27) found that the interplay of interactions of different ranges in the exactly soluble 1-d Ising model can also produce a critical behaviour similar to that described above.

6. INTERACTING SYSTEM OF SPIN, ELECTRONS AND $2K_F$ PHONON

With the above considerations in mind we would like to move on to a determination of the properties of the lattice distortion when both mechanisms are present: the spin-phonon coupling J_1 and the electron-phonon coupling g . It is the Eq. (II, 16) which ties together those two driving forces. In case of $n = 1$ (Ising) and $n = 3$ (Heisenberg) Eq. (II, 16) can be written in terms of hyperbolic functions as follows:

$$\frac{J_1}{2\omega_0} \left[\frac{\sinh 2\beta_c J_1 \Delta}{\cosh 2\beta_c J_1 \Delta + \cosh 2\beta_c J_1 \Delta} \right] + \frac{g^2 \Delta}{2\omega_0} \int_0^{\epsilon_F} d\epsilon N(\epsilon) \frac{\tanh \frac{\beta}{2} \sqrt{\epsilon^2 + (g\Delta)^2}}{\sqrt{\epsilon^2 + (g\Delta)^2}} = \Delta, \quad (n=1) \quad (\text{II}, 34)$$

and

$$\frac{J_1}{2\omega_0} \left[\frac{\sinh 2\beta_c J_1 \Delta}{\cosh 2\beta_c J_1 \Delta - \cosh 2\beta_c J_1 \Delta} + 2 \cdot \frac{2\beta_c J_1 \Delta}{(2\beta_c J_1 \Delta)^2 - (2\beta_c J_1 \Delta)^2} \right] + \frac{g^2 \Delta}{2\omega_0} \int_0^{\epsilon_F} d\epsilon N(\epsilon) \frac{\tanh \frac{\beta}{2} \sqrt{\epsilon^2 + (g\Delta)^2}}{\sqrt{\epsilon^2 + (g\Delta)^2}} = \Delta, \quad (n=3). \quad (\text{II}, 35)$$

It can be seen that in these equations the terms multiplying $\frac{J_1}{2\omega_0} = \Delta_o^s$ are for $T \rightarrow 0$ finite if and only if $J_0 < J_1 \Delta_o$, where $\Delta_o = \Delta(T=0)$.

From Eq.(11,34) we get

$$\Delta_o^s = \Delta_o \left[1 - \frac{g^2 N(0)}{2\omega_0} \text{Arsinh} \frac{\epsilon_F}{g\Delta_o} \right],$$

or upon using Eq.(11,19a) and assuming $\epsilon_F \gg g\Delta_o$ we obtain

$$\Delta_o = \Delta_o^s \left[1 - \frac{\ln \frac{2\epsilon_F}{g\Delta_o}}{\ln \frac{2\epsilon_F}{g\Delta_o^p}} \right]^{-1}. \quad (11,36)$$

For $g \rightarrow \infty, \Delta_o \gg \Delta_o^p$ and $\Delta_o^s / \Delta_o \rightarrow 0$ and
for $g \rightarrow 0, \Delta_o \gg \Delta_o^p$ and $\Delta_o \rightarrow \Delta_o^s$ ($J_1 \neq 0$).

For $J_1 = 0$ we recover results of Eq. (18).

The overall behaviour of Δ for $T=0$ can be summarized as follows:

$$g=0, J_1 \neq 0 : \Delta(0) = \begin{cases} \Delta_o^s = \frac{J_1}{2\omega_0} & \text{if } J_0 < \frac{J_1^2}{4\omega_0} \\ 0 & \text{otherwise,} \end{cases} \quad (11,37a)$$

$$g \neq 0, J_1 = 0 : \Delta(0) = \Delta_o^p = 2\epsilon_F \exp\left(-\frac{1}{g^2 N(0)}\right), \quad (11,37b)$$

$$g \neq 0, J_1 \neq 0 : \Delta(0) = \begin{cases} \Delta_o = \Delta_o^s \left(1 - \frac{\ln \frac{2\epsilon_F}{g\Delta_o}}{\ln \frac{2\epsilon_F}{g\Delta_o^p}}\right)^{-1} & \text{if } J_0 < J_1 \Delta_o f(\Delta_o) \\ \Delta_o^p & \text{otherwise} \end{cases} \quad (11,37c)$$

(11,37d)

Because in Eq.(11,37c) Δ_o is given only implicitly, we were not able to calculate the factor $f(\Delta_o) < 1$ analytically. It is however determined

by the condition that the ground state of (11,37c) is less than that of (11,37d).

Calculation of the second order transition temperature is done as usually but is possible in analytic form only for $J_0 = 0$.

Expanding then Eq. (11,34) for small Δ we find ($n=1$)

$$\frac{J_1^2 \beta_c}{2\omega_0} + \frac{g^2 N(0)}{2\omega_0} \int_0^{\epsilon_F} d\epsilon \tanh \frac{\beta_c \epsilon}{2} = 1, \quad (J_0=0). \quad (11,38)$$

Denoting $T_c^{(1)} = J_1^2 / 2\omega_0$ and observing that $\frac{g^2 N(0)}{2\omega_0} = \ln \frac{1.14 \epsilon_F}{T_p}$ (Eq. 11,18a)) we rewrite (11,38) as

$$T_c = T_c^{(1)} \left(1 - \frac{\ln \frac{1.14 \epsilon_F}{T_c}}{\ln \frac{1.14 \epsilon_F}{T_p}} \right)^{-1}, \quad (11,39)$$

so as an analogue of Eq. (11,37) the following relations result:

$$g=0, J_1 \neq 0: T_c = \begin{cases} T_c^{(n)}(J_0, J_1, \omega_0) & J_0 < J_1^2 / 4\omega_0 \\ 0 & \text{otherwise} \end{cases}, \quad (11,40a)$$

$$g \neq 0, J_1 = 0: T_c = T_p = 1.14 \epsilon_F \exp\left(-\frac{1}{\frac{g^2 N(0)}{2\omega_0}}\right), \quad (11,40b)$$

$$g \neq 0, J_1 \neq 0: T_c = \begin{cases} T_c^{(n)}(J_0, J_1, \omega_0) \cdot \left(1 - \frac{\ln \frac{1.14 \epsilon_F}{T_c}}{\ln \frac{1.14 \epsilon_F}{T_p}} \right)^{-1} & \text{if } J_0 < J_1 \Delta_c f(\Delta_c) \\ T_p & \text{otherwise} \end{cases} \quad (11,40c)$$

(11,40d)

The dependence of $\Delta(0)$ and T_c on J_0 is illustrated schematically in Figs. 78 and 9 respectively. Note that in our approximation T_p remains

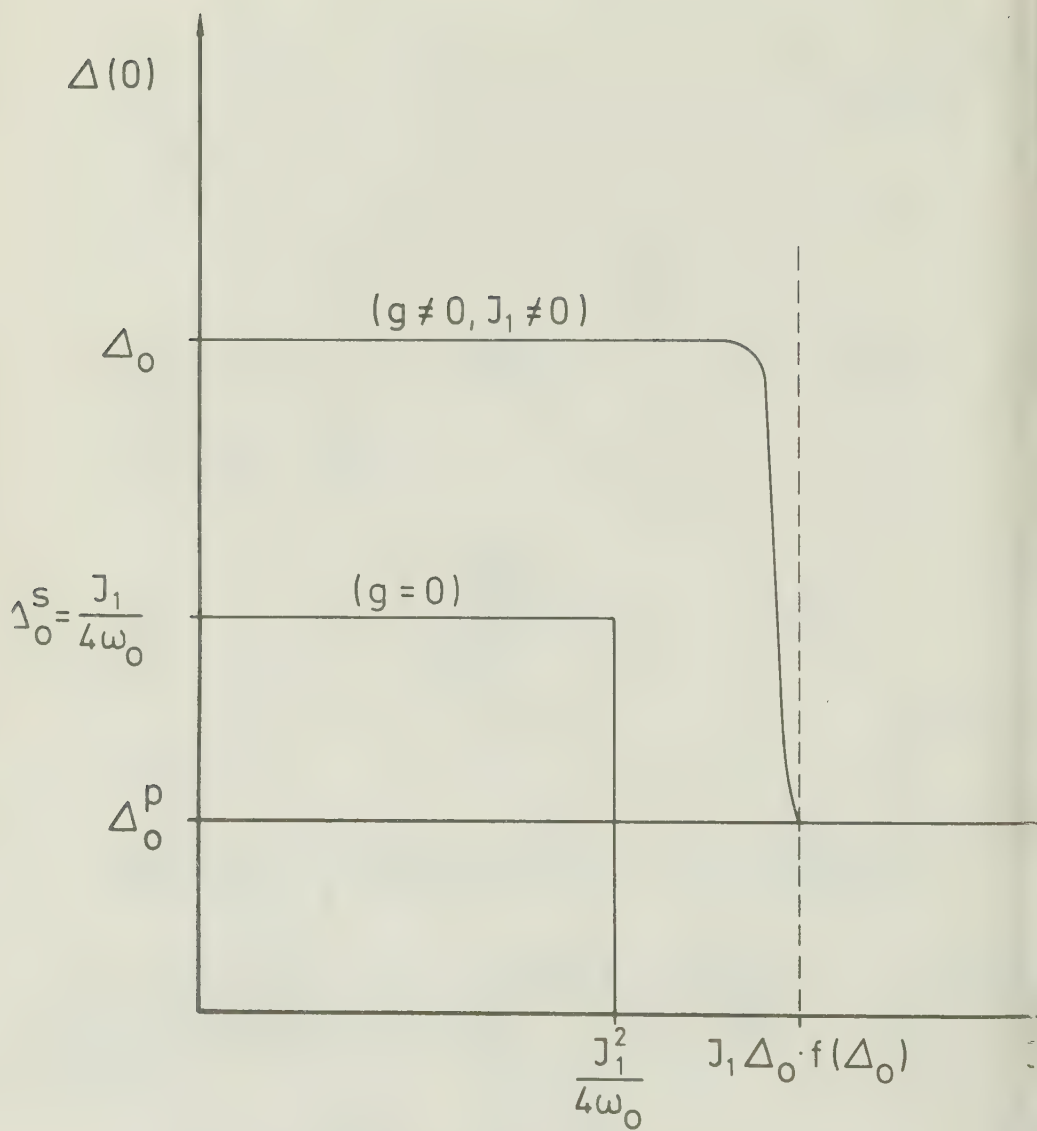


Fig. 7: $T = 0$ values of the lattice distortion Δ as a function of J_0 for $\Delta_o^s < \Delta_o^p$

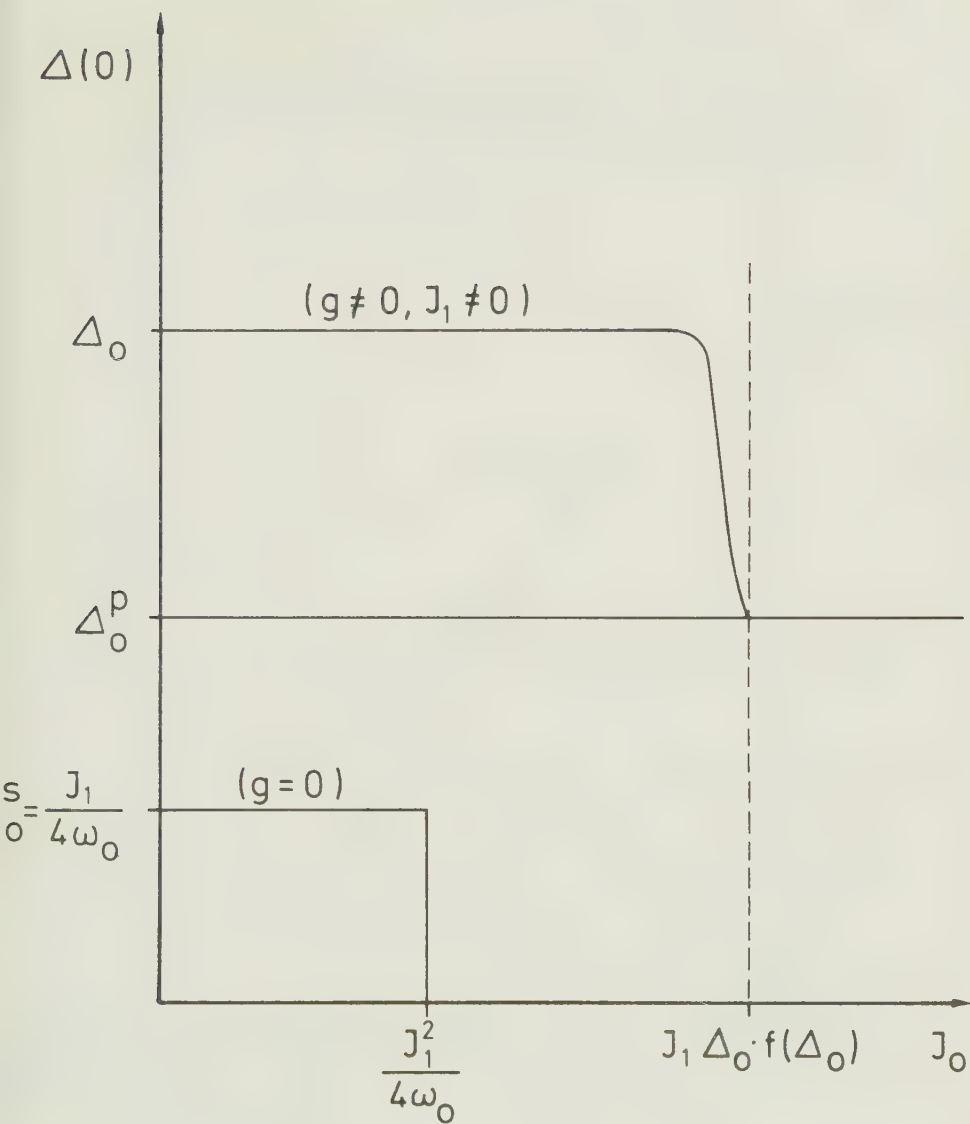


Fig. 8: $T = 0$ values of the lattice distortion Δ as a function of J_0 for $\Delta_0^s < \Delta_0^p$

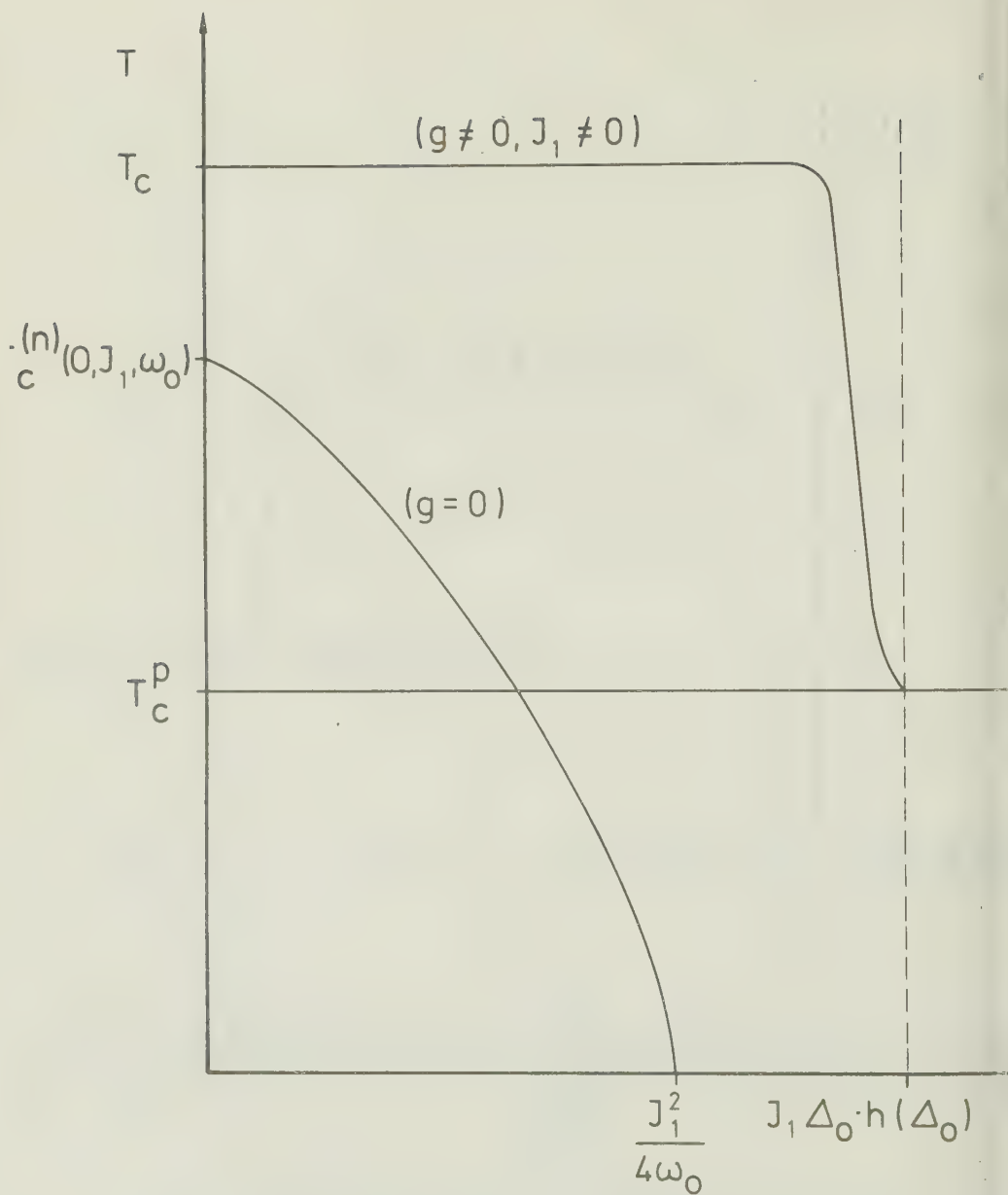


Fig. 9: Critical temperatures of the lattice distortion for $g = 0$ and $g \neq 0$.

For $J_0 > J_1 \Delta_0 h(\Delta_0) [h(\Delta_0 < 1)]$, $T_c \rightarrow T_c^p$

independent from J_0 . By increasing J_0 only the contribution to $\Delta(0)$ (and to T_C) due to the spin-phonon coupling is decreased and eventually for J_0 large enough the J_1 coupling ceases to have any effect on the lattice distortion.

7. CONCLUSIONS AND DISCUSSIONS

The aim of the present Chapter is to gain some insight into the physics of quasi one-dimensional systems of interacting electrons, phonons and spins by means of a simple model. In order to obtain a mathematically tractable theory only the most significant features of the real systems could be incorporated in the model. At first we have used just one phonon mode interacting with electrons and spins. This phonon has the wave vector $K = 2k_F$ and is most strongly influenced by electrons at the Fermi energy. Because we are interested only in static properties the quantum nature of the phonon can be neglected at $T \neq 0$ and it can be treated classically. Clearly, when all lattice degrees of freedom are excitable then the $q = 2K_F$ mode is only defined within the molecular-field theory, which breaks down in 1-d. However, although there exists perhaps no long range order for $T \neq 0$ and therefore no gaps, the increasing sizes of the fluctuation domains with $2K_F$ -distortion produce effects similar to those of real gaps. On the same footing the approximation to treat the spins classically is perfectly justified as long as one is interested in a crude picture of static properties.

In view of the approximative nature of the model studied it is obvious that the phase diagram obtained for the system is only a shadow of a more complex thermodynamic structure. In fact, a rigorous analysis of the simple Ising model coupled linearly to the lattice and subject to periodic boundary conditions (28) shows at $T = 0$ a phase transition to a ferro-

(antiferro-) magnetically ordered state only for $|J_0| > J_1^2/2\omega_0$, whereas for $|J_0| < J_1^2/2\omega_0$ the ground state is disordered on the long range scale. However, the long range ordered dimerized ground state $[1/N \langle \sum_i \vec{S}_i \cdot \vec{S}_{i+1} \rangle = 0]$ obtained for the Ising-spin-one-phonon problem for $|J_0| < J_1^2/4\omega_0$ is reflected in the Ising all-phonon problem in the appearance of a short-range-order parameter $\langle \frac{1}{N} \sum_i \vec{S}_i \cdot \vec{S}_{i+1} \rangle = 2J_0\omega_0/J_1^2$. The latter quantity shows the degree of dimerization realized in the system.

Let us point out that for $n = 1$ our equations can be mapped into the theory of Blume et al ⁽²⁴⁾ and for general n we obtain other, non trivial examples of the cross-over between the second and first order phase transitions. This had to be expected on quite general grounds since we are faced with the competition of non ordering (here spins) and ordering (here lattice distortions) densities. This competition can lead to the change of the order of transition.

The magnetic models considered here do not show spontaneous magnetization for any finite temperature. The spin-spin correlations have, however, a pronounced effect on the lattice distortion. For vanishing electron-phonon coupling the strong spin coupling pushes the appearance of lattice distortions to lower temperatures and eventually destroys it. In the more general case the spin correlations can make the spin-phonon coupling completely ineffective for producing a lattice distortion.

This behaviour is presumably of a general nature and will show up also in a more extensive approach to phonon

variables. It will probably also appear in a more realistic treatment of quasi one-dimensional systems where the long range order is achieved via interchain coupling. In this respect the situation that the spin system has a finite critical temperature is of particular interest, specifically with respect to its influence on the nature of the Peierls transition.

We would like to point out that in systems like N-methyl-phenazinium-tetracyanoquinodimethane (NMP-TCNQ), where the Coulomb repulsion is of the same order of magnitude as the hopping energy ⁽²⁹⁾ (and this gives rise to localized moments), the spin and electron operators cannot be treated independently. In this case a classical spin approximation is not permissible and a similar treatment to that of Pytte ⁽¹⁷⁾ for the $S = \frac{1}{2}$ antiferromagnetic Heisenberg chain is more suited. In the case where the electron system exhibits the antiferromagnetic ground state, as in (NMP-TCNQ), the theory of Pytte ⁽¹⁷⁾ shows, that a Peierls transition can be expected owing to spin-lattice interaction having a periodicity determined by the magnitude of the applied magnetic field. One would then have a potential Peierls instability due to the electron-lattice interaction with $2K_F$ periodicity.

In order to clarify further the relation between the present model and the $S = \frac{1}{2}$ Heisenberg model discussed by Pytte some additional remarks will be made. Considering the Ising-spin-one-phonon case one can write the energy of the chain in the form ($T = 0$)

$$E = -\sum_l [J_0 + (-1)^l J_1(\Delta^2)\Delta + \frac{1}{2} J_2(\Delta^2)\Delta^2] \vec{S}_l \cdot \vec{S}_{l+1} + E_{ph}, \quad (11,41)$$

where J_1 and J_2 are functions of Δ^2 characterizing anharmonic spin lattice coupling. From Eq. (11) it follows that the odd term $\sim \Delta$ drops for ferromagnetic or antiferromagnetic ordering. Therefore, for $J_2=0, J_1(\Delta^2)=J_1$, and $|J_0| > J_1^2/4\omega_0$, $\Delta=0$ is the stable solution and no distortion of the chain can occur. Only if J_1 or J_2 are Δ^2 dependent a distortion of the chain when it is ferromagnetically or antiferromagnetically ordered is possible. The latter two cases will not be discussed further. In contrast to the case discussed so far a dimerized spin configuration will yield a linear term $\sim \Delta$ in Eq. (11,41) and for $|J_0| \leq J_1^2/4\omega_0$, $\Delta \neq 0$ is a solution. This situation is illustrated in Fig. 10.

In order to discuss the $S = \frac{1}{2}$ Heisenberg model from the same point of view one should notice that the antiferromagnetic ground state of the $S = \frac{1}{2}$ system deviates from the classical antiferromagnetic ordering of alternating spins owing to quantum effects. This implies, for example, that neighbouring spins are parallel oriented with nonvanishing probability. Accordingly, in Eq. (11,41) the linear term in Δ will not always vanish. Consequently already for $J_1^2/4\omega_0 |J_0| \ll 1$ a distortion of the chain will occur. This has been shown by Pytte (17) by going over to a Fermion representation. Let us point out that once the electron-lattice coupling is turned on a distortion occurs at $T = 0$ irrespective of the ratio $J_1^2/4\omega_0 |J_0|$. On account of our arguments one expects that

the ferromagnetic $S = \frac{1}{2}$ system does not have a lattice distortion for $J_1^2/4\omega_0 \ll 1$. The argument is roughly as follows. The parallel ordered spin state is an exact eigenstate of the system. That it is also the ground state of the system, at $T = 0$ requires that the excitation spectrum be definite. For $|J_0| < J_1^2/4\omega_0$ an instability of the $S = \frac{1}{2}$ system to a dimerized spin configuration can be expected which arises over short wave length excitations. These have finite energy for $J_0 > 0$ and $J_1 = 0$. Accordingly, one expects that for $J_1^2/4\omega_0 |J_0| \ll 1$ the positive character of the excitations from the parallel ordered state is not changed. Since in the distorted parallel ordered state no energy can be gained it is concluded that for $S = \frac{1}{2}$ and $J_0 > 0$, in the limit $J_1^2/4\omega_0 |J_0| \ll 1$ the parallel ordered undistorted state is the ground state at $T = 0$.

It is understood that in Fig. 10 the spin configuration drawn for $S = \frac{1}{2}$ and $J_0 < 0$ is schematic owing to quantum deviations. It can be expected that for $|J_0| < J_1^2/4\omega_0$ the spin lattice configuration for the $S = \frac{1}{2}$ system will be analogous to the classical one. Eventually we point out that for $S \rightarrow \infty$, i.e. when the spin gets classical, the lattice distortion for $J_0 < 0$ and $J_1^2/4\omega_0 |J_0| \ll 1$ will vanish.

Finally, we would like to confront the appearance of the phase transition in our one-dimensional model with the general criteria for the phase transitions in one dimension (30).

It is well known that the occurrence of a phase tran-

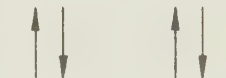
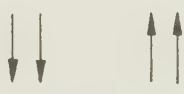
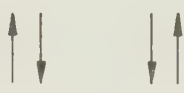
	$J_0 > 0$	$J_0 < 0$
ISING $n=1$ $ J_0 > J_1^2/4\omega_0$		
HEISENBERG $S = \frac{1}{2}$		
$ J_0 \leq J_1^2/4\omega_0$ ISING $n=1$ $J_1 > 0$ $J_1 < 0$	 	 

Fig. 10: Ground state spin-lattice configurations of Ising spin-lattice and Heisenberg $S = 1/2$ lattice system.

sition in a one-dimensional system requires the existence of an infinite-range interaction (30). Such an interaction is exemplified in conventional molecular field theories or in the magnetic models where the exchange interaction is of long ranged functional form. In our Hamiltonian there are no such interactions since the spin Hamiltonian is clearly short range and the lattice elastic energy is obviously classical in nature.

The long range interaction potential enters indirectly from the kinematical restrictions imposed on possible lattice configuration.

For example, if we took a lattice configuration with $\Delta > 0$ associated with the first ion and then reversed its sign $\Delta \rightarrow -\Delta$, then all the distortion up to the Nth ion would reverse their signs. This is a cooperative effect of infinite range and one should not be surprised at the occurrence of the phase transition.

Chapter III

SPIN-PEIERLS TRANSITION IN QUANTUM

S = 1/2 X-Y SPIN SYSTEMS*)

*) Major portions of this Chapter will be presented during the International Conference on Magnetism, Amsterdam, September 1976 (Proceedings thereof to be published in Physica (1977)).

1. INTRODUCTION

In the previous Chapter we have investigated the Peierls transition in coupled electron and classical spin systems. Because we have limited ourselves to the interaction of the electron and spin systems, respectively, with a single lattice mode, we could treat the problem exactly: both electron lattice and spin-lattice subsystems could be rigorously solved.

In this Chapter we are going to analyse the quantum mechanical analogue of the $n = 2$ classical spin system - the spin 1/2 X-Y model (31) interacting with the lattice. We expect that the quantum nature of the model will affect some of the results obtained in Chapter II.

The X-Y model derives its name from its form

$$H_{X-Y} = - \sum_{\langle ij \rangle} (J_{ij}^x S_i^x S_j^x + J_{ij}^y S_i^y S_j^y) \quad , \quad (III.1)$$

where S_i^x and S_i^y are quantum mechanical operators, components of the spin 1/2 operator $\vec{S} = (S^x, S^y, S^z)$. The components of $\vec{S}$ satisfy the usual angular momentum commutation rules and can be represented by Pauli matrices.

The spin 1/2 quantum X-Y model is particularly interesting as perhaps the simplest possible fully quantum mechanical many-body system. Its exact solution for general anisotropic case ($J^x \neq J^y$) in the presence of magnetic field was given for 1-d by Lieb, Schultz

and Mattis⁽³¹⁾.

In this Chapter we are going to explore the behaviour of the lattice distortion which originates from the Hamiltonian (III,1) in 1-d in which the spin-lattice coupling was explicitly taken into account. We shall treat a general anisotropic case with $J_{ij}^{\alpha} (\alpha=X,Y)$ developed up to second order in Δr_{ij} . The spin-lattice interaction with the single $q = \frac{\pi}{a}$ mode of the harmonic lattice leads to the sign alternation of part of resulting lattice dependent exchange constant, in a close analogy to the treatment of Chapter II. The exact expression for the partition function of such an alternating anisotropic, lattice-dependent X-Y model will be derived as an extension of results of Lieb et al.⁽³¹⁾. The self-consistent equations for the spin-lattice coupling driven lattice distortion (spin-Peierls transition⁽¹⁴⁾) will be discussed as a function of parameters involved. It will be shown that the quantum nature of the problem brings about important differences as compared to the analogous classical model of Chapter II: the spin-Peierls transition in the X-Y model is always of second order, irrespective of the lattice-independent part of exchange J_0 . Furthermore, it is proven that the ground state ($T = 0$) of the X-Y chain is always distorted, even for infinitesimally small spin-lattice coupling.

In Section 2 we write down the Hamiltonian of the system and discuss its relation to the theoretical treatments of similar models.

In Section 3 we calculate the energy spectrum of the Hamiltonian in which we use the Jordan-Wigner transformation between spin operators and spinless fermion operators. The resulting quasi-fermion Hamiltonian is diagonalized by the generalization of Bogoliubov-Valatin transformation. This enables us to write down an exact expression for the partition function of the system.

In Section 4 we analyze the thermodynamic properties of the lattice distortion which follow from the minimization of the exact free energy. Self-consistency integral equation for the lattice distortion is discussed and solved exactly for limiting cases of vanishing anisotropy and vanishing spin-lattice interaction. The Landau expansion of the free energy is constructed and the order of the transition is discussed. The ground state energy is calculated and the form of the ground state of the chain is derived.

In Section 5 we give a short discussion of results obtained with the particular emphasis on the comparison with the results of Chapter II.

2. THE HAMILTONIAN OF THE SYSTEM

Consider a one-dimensional system of N $S = \frac{1}{2}$ quantum spins interacting through the Hamiltonian of the form (III,1). We assume only nearest neighbor interaction. For a general anisotropic case we rewrite (III,1) as

$$H_{x-y} = - \sum_l J_{l,l+1} [(1+\gamma') S_l^x S_{l+1}^x + (1-\gamma') S_l^y S_{l+1}^y] , \quad (\text{III},2)$$

where γ' is as yet not specified anisotropy constant. $\gamma' = 0$ corresponds to the fully isotropic case of (III,1). Further, we assume that the ions with spins are allowed to deviate from their equilibrium positions R_l^0 and by u_l we denote the deviation of the l -th ion from R_l^0 . The coupling constant is assumed to be a function of the distance between the ions. We expand now $J_{l,l+1}$ as in the Chapter II, keeping only the linear terms in $u_l - u_{l+1}$

$$J_{l,l+1} = J_0 + J_1 \cdot (u_l - u_{l+1}), \quad J_1 \equiv \nabla J_{l,l+1}. \quad (\text{III},3)$$

We perform now the Fourier transformation of the lattice variables u_l and we keep only the term with $q = \frac{\pi}{a}$, where a is the lattice constant. We obtain then

$$H_{x-y} = - \sum_l \left[J_0 + (-1)^l J_1 \Delta \right] \left[(1 + \gamma') S_l^x S_{l+1}^x + (1 - \gamma') S_l^y S_{l+1}^y \right], \quad (\text{III},4)$$

where $\Delta \equiv u_{q=\frac{\pi}{a}}$ i.e. Δ is the periodic lattice distortion with $q = \frac{\pi}{a}$. The spin-lattice interaction J_1 causes the sign alternation of the part of the exchange interaction between the neighboring spins. In the form (III,4) of the Hamiltonian H_{x-y} there is no relation between the direction of the chain and the directions of axes of the spin system. The spin-lattice interaction influences the exchange in the same way for both spin components. We shall now assume that the anisotropy constant γ' is itself a function of Δ , $\gamma' = \gamma'(\Delta)$. More specifically, let us adopt the simplest form of

$$\gamma'(\Delta)$$

$$\gamma'(\Delta) = \gamma \cdot \Delta, \quad (III, 5)$$

where γ is another constant. In other words, we have assumed that the anisotropy in the exchange appears only as a result of the periodic lattice distortion, being proportional to it with the proportionality constant γ . (We can associate the spin x axis with the direction of the chain.) We rewrite (III,4) now as

$$H_{x-y} = - \sum_l [J_l^x(\Delta) S_l^x S_{l+1}^x + J_l^y(\Delta) S_l^y S_{l+1}^y], \quad (III, 6)$$

with

$$J_l^x(\Delta) = J_0 + \Delta [(-1)^l J_1 + \gamma J_0] + (-1)^l J_1 \gamma \Delta^2 \quad (III, 7a)$$

and

$$J_l^y(\Delta) = J_0 + \Delta [(-1)^l J_1 - \gamma J_0] - (-1)^l J_1 \gamma \Delta^2. \quad (III, 7b)$$

Eqs. (III,7a) and (III,7b) indicate that with the form (III,5) we have practically expanded the exchange constants $J_l^x(\Delta)$ and $J_l^y(\Delta)$ up to second order in Δ , with different expansion coefficients for J^x and J^y . For $J_1 = 0$ one has a conventional, anisotropic X-Y

model⁽³¹⁾, whereas for $\gamma=0$ one has an "alternating", isotropic X-Y model. In the next section we are going to show that also in the case $J_1 \neq 0, \gamma \neq 0$ the Hamiltonian (III,6) is exactly soluble. It will then provide the means for studying $\Delta=\Delta(T)$ resulting from this exactly soluble generalization of the X-Y model.

3. CALCULATION OF THE ENERGY SPECTRUM OF THE HAMILTONIAN H_{x-y}

In order to find the energy spectrum of H_{x-y}

$$H_{x-y} = - \sum_l [J_0 + (-1)^l J_1 \Delta] [(1+\gamma\Delta) S_l^x S_{l+1}^x + (1-\gamma\Delta) S_l^y S_{l+1}^y] \quad (\text{III},8)$$

we first use the representation of the spin operators in terms of so-called Pauli operators a_l ,

$$S_l^x = \frac{1}{2}(a_l^+ + a_l), \quad S_l^y = \frac{1}{2i}(a_l^+ - a_l), \quad S_l^z = a_l^+ a_l - \frac{1}{2} \quad (\text{III},9)$$

One can satisfy the angular momentum commutation rules, if the a_l 's satisfy a "mixed" set of commutation rules

$$\{a_l, a_l^+\} = 1, (a_l^+)^2 = (a_l)^2 = 0, [a_l, a_{l'}^+] = 0, l \neq l', \quad (\text{III},10)$$

i.e. a_l are "locally" fermions and "non-locally" bosons. With the help

of a'_l (III,8) can be rewritten as

$$H_{x-y} = -\frac{1}{2}J_0 \sum_l [a_l^\dagger a_{l+1} + a_{l+1}^\dagger a_l + \gamma \Delta (a_l^\dagger a_{l+1}^\dagger + a_{l+1} a_l)] + \\ -\frac{1}{2}J_1 \Delta \sum_l (-1)^l [a_l^\dagger a_{l+1} + a_{l+1}^\dagger a_l] - \frac{1}{2}\gamma J_1 \Delta^2 \sum_l (-1)^l [a_l^\dagger a_{l+1}^\dagger + a_{l+1} a_l]. \quad (\text{III}, 11)$$

By means of the Jordan-Wigner transformation (see Appendix C) it is possible to rewrite (III,11) in terms of spinless fermion operators C_l defined by

$$C_l = \exp\left(\pi i \sum_{l'=1}^{l-1} a_{l'}^\dagger a_{l'}\right) a_l, \quad C_l^\dagger = a_l^\dagger \exp\left(-\pi i \sum_{l'=1}^{l-1} a_{l'}^\dagger a_{l'}\right) \quad (\text{III}, 12)$$

as

$$H_{x-y} = -\frac{1}{2}J_0 \sum_l [C_l^\dagger C_{l+1} + C_{l+1}^\dagger C_l + \gamma \Delta (C_l^\dagger C_{l+1}^\dagger + C_{l+1} C_l)] + \\ -\frac{1}{2}J_1 \Delta \sum_l (-1)^l [C_l^\dagger C_{l+1} + C_{l+1}^\dagger C_l] - \frac{1}{2}\gamma J_1 \Delta^2 \sum_l (-1)^l [C_l^\dagger C_{l+1}^\dagger + C_{l+1} C_l]. \quad (\text{III}, 13)$$

Since (III,13) is a general quadratic form in fermion operators and is evidently hermitian, it can be diagonalized by an appropriate unitary transformation. To this end, it is useful to introduce the Fourier transform $C_q^\dagger$ of $C_l^\dagger$

$$C_l^\dagger = N^{-\frac{1}{2}} \sum_q e^{-iql} C_q^\dagger, \quad (\text{III}, 14)$$

where $q = 0, \pm \frac{2\pi}{N}, \pm \frac{4\pi}{N}, \dots, \pm \frac{(N-2)\pi}{N}, \pi$ ($a \equiv 1$).

In terms of C_q^+ 's (III,13) reads

$$\begin{aligned} H_{X-Y} = & - \int_0^{\infty} \sum_{\pi > q > 0} \left[\cos q (C_q^+ C_q + C_{-q}^+ C_{-q}) + i \gamma \Delta \sin q (C_q^+ C_{-q}^+ + C_q C_{-q}) \right] + \\ & + i \int_0^{\infty} \Delta \sum_{\pi > q > 0} \sin q (C_q^+ C_{q-\pi} - C_{q-\pi}^+ C_q) + \\ & + \frac{\gamma \Delta^2}{2} \sum_{\pi > q > 0} \left[e^{-iq} (C_q^+ C_{q-\pi}^+ - C_q C_{\pi-q}) + e^{iq} (C_q^+ C_{\pi-q}^+ - C_q C_{q-\pi}) \right]. \quad (\text{III},15) \end{aligned}$$

One can see directly from (III,15) that the linear combinations of operators of the type

$$\alpha_q^{(i)+} = a_q^{(i)} C_q^+ + b_q^{(i)} C_{-q} + d_q^{(i)} C_{q-\pi}^+ + e_q^{(i)} C_{\pi-q}, \quad (i=1, \dots, 4) \quad (\text{III},16)$$

where $a_q^{(i)}$, $b_q^{(i)}$, $d_q^{(i)}$ and $e_q^{(i)}$ are constants to be determined, will diagonalize (III,15). This is a generalization of the Bogoliubov-Valatin transformation. We shall be concerned here with the eigenvalue spectrum of (III,15) and we will not find its eigenvectors, which is a laborious task. In the basis $\Psi^* = (C_q^+, C_{-q}, C_{q-\pi}^+, C_{\pi-q})$ the Hamiltonian H_{X-Y} has the form

$$H_{X-Y} = \Psi^* \hat{H}_{X-Y} \Psi, \quad (\text{III},17)$$

where the matrix $\hat{H}_{x-y}$ takes on the following form:

	c_q	c_{-q}^+	$c_{q-\pi}$	$c_{\pi-q}^+$
c_q^+	$-\int_0 \cos q$	$-i\chi_1 \Delta \sin q$	$i\int_1 \Delta \sin q$	$\chi_1 \Delta^2 \cos q$
c_{-q}	$i\chi_0 \Delta \sin q$	$\int_0 \cos q$	$-\chi_1 \Delta^2 \cos q$	0
$c_{q-\pi}^+$	$-i\int_1 \Delta \sin q$	$-\chi_1 \Delta^2 \cos q$	$\int_0 \cos q$	$i\chi_0 \Delta \sin q$
$c_{\pi-q}$	$\chi_1 \Delta^2 \cos q$	0	$-i\chi_0 \Delta \cos q$	$-\int_0 \cos q$

(III, 18)

In deriving (III,18) we have used the fermion commutation relations to determine the signs of the matrix elements.

Denoting

$$\alpha = \int_0 \cos q, \quad ,$$

$$\epsilon = i\int_1 \Delta \sin q$$

(III, 19)

$$\beta = i\chi_0 \Delta \sin q, \quad ,$$

$$\delta = \chi_1 \Delta^2 \cos q$$

the secular equation $\det(\hat{H}_{x-y} - \lambda I)$ can be written

$$\det \begin{pmatrix} -\alpha - \lambda & \beta & \epsilon & \delta \\ \beta & \alpha - \lambda & -\delta & \epsilon \\ -\epsilon & -\delta & \alpha - \lambda & \beta \\ \delta & \epsilon & -\beta & -\alpha - \lambda \end{pmatrix} = 0$$

and the resulting equation reads

$$\lambda^4 + [-2(\alpha^2 + \delta^2 - \beta^2) + \epsilon^2]\lambda^2 + [(\alpha^2 - \beta^2 + \delta^2)^2 - \epsilon^2\alpha^2 + 4\delta\epsilon(\beta\epsilon - \delta\alpha)] = 0, \text{ (III, 20)}$$

with the following four real solutions

$$\lambda_{1,2,3,4} = \pm \left\{ \alpha^2 + \delta^2 - \beta^2 - \frac{\epsilon^2}{2} \pm \left[4\alpha\delta(\alpha\delta - \beta\epsilon) + (\beta^2 - \delta^2)\epsilon^2 + \frac{\epsilon^4}{4} \right]^{\frac{1}{2}} \right\}^{\frac{1}{2}}, \text{ (III, 21)}$$

which using the definitions (III,19) become

$$\lambda_{1,2,3,4}(q) = \pm (A_q \pm B_q)^{1/2}, \quad (\text{III}, 22)$$

where

$$A_q = (J_0^2 + \gamma^2 J_1^2 \Delta^4) \cos^2 q + \Delta^2 (\gamma^2 J_0^2 + \frac{1}{2} J_0^2) \sin^2 q \quad (\text{III}, 23)$$

and

$$B_q = \Delta^2 |J_1| \left[4 \gamma^2 J_0^2 \cos^2 q + \gamma^2 \sin^2 q (J_1^2 \Delta^2 \cos^2 q + J_0^2 \sin^2 q) + \frac{J_1^2}{4} \sin^4 q \right]^{1/2} \quad (\text{III}, 23)$$

where $0 < q < \pi$.

The signs in (III,22) are determined by the requirement that the spectrum (III,22) for $J_1 \rightarrow 0$ and $\gamma \rightarrow 0$ goes smoothly over to the known spectrum of the isotropic X-Y model, which is ⁽³¹⁾

$\lambda(q) = J_0 \text{sgn}(\cos q) \cos q$ for $0 < q < \pi$. This is equivalent to the constraint

$$\lambda(q) = \text{sgn}(\cos q) (A_q + B_q)^{1/2}, \quad 0 < q < \pi. \quad (\text{III}, 24)$$

The quasi fermion spectrum (III,24) possesses a gap at $q = \frac{\pi}{2}$ in full analogy to the Peierls gap in the electronic spectrum of Chapter II,

This gap Δ_t can be calculated from (III,24) to give

$$\Delta_t = \Delta \left[(\gamma^2 J_0^2 + \frac{1}{2} J_1^2) + |J_1| (\gamma^2 J_0^2 + \frac{J_1^2}{4})^{\frac{1}{2}} \right]^{\frac{1}{2}}, \quad (\text{III},25)$$

which for $\gamma=0$, $J_1 \neq 0$ (only alternation) reduces to $\Delta_t = \Delta_1 = J_1 \Delta$ and for $\gamma \neq 0$, $J_1 = 0$ (only anisotropy) reduces to $\Delta_t = \Delta_2 = \Delta \gamma J_0$. These two mechanisms, the alternation of the exchange constant and the anisotropy contribute collectively to the total gap (III,25).

The energy spectrum (III,24) is schematically depicted in the Fig.11.

Let us also write down for completeness the limiting cases of the spectrum (III,24) for $J_1 \neq 0, \gamma=0$

$$\lambda(q) = \text{sgn}(\cos q) (J_0^2 \cos^2 q + J_1^2 \Delta^2 \sin^2 q)^{\frac{1}{2}}, \quad (\text{III},26a)$$

and for $J_1=0, \gamma \neq 0$

$$\lambda(q) = \text{sgn}(\cos q) [J_0 \cos^2 q + \gamma^2 \Delta^2 \sin^2 q]^{\frac{1}{2}}. \quad (\text{III},26b)$$

Given the expression (III,24) we are able to write down the partition function of the system and consequently all the thermodynamical potentials,

In particular, the total free energy per spin, including the elastic potential energy $\omega_0 \Delta^2$ is

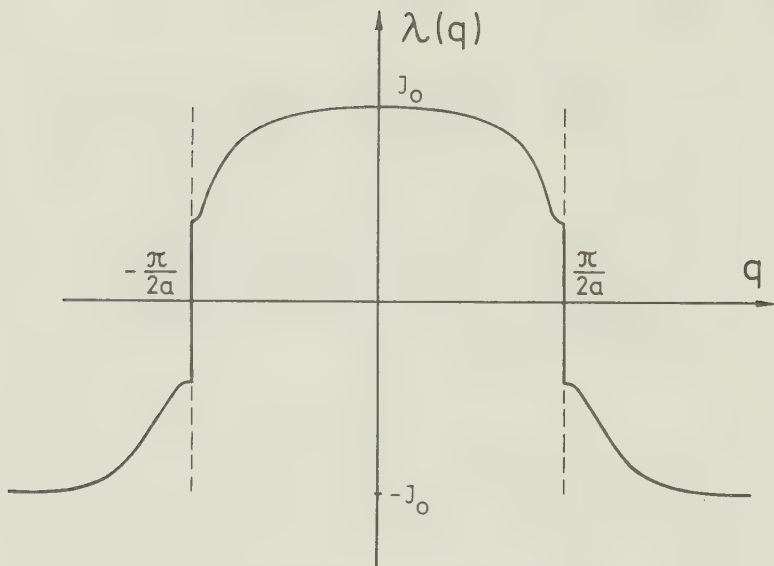


Fig. 11: Energy spectrum of the X-Y model

$$\begin{aligned} \psi(\Delta, T) &= \psi_0 + \omega_0 \Delta^2 \\ -2(\beta\pi)^{-1} \int_0^{\frac{\pi}{2}} dq \ln \cosh \frac{\beta}{2} \{ &(\Delta_0^2 + \gamma^2 J_1^2 \Delta^4) \cos^2 q + \Delta^2 (\gamma^2 J_0^2 + \frac{1}{2} J_1^2) \sin^2 q \\ &+ |J_1| \Delta^2 [4\gamma^2 J_0^2 \cos^2 q + \gamma^2 \sin^2 q (J_1^2 \Delta^2 \cos^2 q + J_0^2 \sin^2 q) + \frac{1}{4} J_1^2 \sin^4 q] \}^{\frac{1}{2}} \}^{\frac{1}{2}}. \end{aligned} \quad (\text{III}, 27)$$

From the exact expression (III,27) all the physical informations can be extracted. In the next Section we shall examine the critical and ground state properties of Δ resulting from the minimization of $\psi(\Delta, T)$.

4. GROUND STATE AND CRITICAL PROPERTIES OF THE LATTICE DISTORTION

We shall now examine the $T = 0$ ground state properties of the lattice distortion which originates from (III,27).

The ground state energy per spin e_0 is obtained as $\beta \rightarrow \infty$ limit of the internal energy $e = \frac{\partial}{\partial \beta} (\beta \psi(\Delta, \beta))$ and is equal to

$$\begin{aligned} e_0 &= -\frac{1}{\pi} \int_0^{\frac{\pi}{2}} dq \{ (\Delta_0^2 + \gamma^2 J_1^2 \Delta^4) \cos^2 q + \Delta^2 (\gamma^2 J_0^2 + \frac{1}{2} J_1^2) \sin^2 q \\ &+ |J_1| \Delta^2 [4\gamma^2 J_0^2 \cos^2 q + \gamma^2 \sin^2 q (J_1^2 \Delta^2 \cos^2 q + J_0^2 \sin^2 q) + \frac{1}{4} J_1^2 \sin^4 q] \}^{\frac{1}{2}} \}^{\frac{1}{2}} \\ &+ \omega_0 \Delta^2. \end{aligned} \quad (\text{III}, 28)$$

Unfortunately, the integral in (III,28) cannot be analytically evaluated except for special cases. For example, for $\gamma=0$, $J_1 \neq 0$

$$e_o^{(d)} = -\frac{1}{\pi} \int_0^{\frac{\pi}{2}} dq \left\{ J_0^2 \omega_s^2 q + J_1^2 \Delta^2 \sin^2 q \right\}^{\frac{1}{2}} + \omega_o \Delta^2 =$$

$$= -\frac{|J_0|}{\pi} E(k_d(\Delta)) + \omega_o \Delta^2 \quad (\text{III}, 29)$$

where $E(x)$ is the complete elliptic integral of the second kind⁽³²⁾ and $k_d = (1 - J_1^2 \Delta^2 / J_0^2)^{\frac{1}{2}}$.

In order to find the $T = 0$ lattice distortion Δ_o we must minimize (III,29) with respect to Δ . We use the asymptotic series representation of $E(x)$ ⁽³²⁾

$$E(k_d) \approx 1 + \frac{1}{2} (2 \ln 2 - \ln k_d' - \frac{1}{2}) k_d'^2 + \dots, \quad (\text{III}, 30)$$

where $k_d' = (1 - k_d^2)^{\frac{1}{2}} = J_1 \Delta / J_0$.

By substituting (III,30) into (III,29) and by minimizing it with respect to Δ one obtains for $|J_0| > J_1^2 / \omega_o$

$$\Delta(T=0) = \Delta_o \approx \frac{|J_0|}{J_1} \exp \left[- \left(\frac{1}{2} - \ln 2 + \frac{\pi}{4} \frac{\omega_o |J_0|}{J_1^2} \right) \right]. \quad (\text{III}, 31)$$

We conclude that by increasing $|J_0|$ Δ exponentially decreases, but never becomes zero. Therefore, the distorted X-Y chain has at $T = 0$ always lower energy than the undistorted one. Similar calculations can be performed for $\gamma \neq 0, J_1 = 0$ with

$$e_o^{(a)} = -\frac{|J_0|}{\pi} E(k_a(\Delta)) + \omega_o \Delta^2, \quad (\text{III}, 29a)$$

where $k_a = \gamma \Delta$. We observe that the logarithmic in Δ terms will always exist in the expansion of (III,28) thereby guaranteeing the exponential decrease of Δ_0 with increasing $|\mathcal{J}_0|$. The comparison of $\Delta_0(\mathcal{J}_0)$ for classical and quantum cases is illustrated in the Fig. 12.

Let us now consider the behavior of Δ for finite temperatures. By setting $\frac{\partial \mathcal{F}}{\partial \Delta} = 0$ using (III,27) we obtain the following integral equation for $\Delta(T)$

$$(\beta \pi)^{-1} \frac{\partial}{\partial \Delta} \int_0^{\frac{\pi}{2}} dq \ln \cosh \frac{\beta}{2} [A_q(\Delta) + B_q(\Delta)]^{\frac{1}{2}} = \omega_0 \Delta \quad (\text{III},32)$$

where $A_q(\Delta)$ and $B_q(\Delta)$ are given by (III,23a) and (III,23b). By again expanding (III,32) for small Δ we obtain the following implicit equation for $T_c = T_c(\mathcal{J}_0, \mathcal{J}_1, \gamma, \omega_0)$

$$\frac{1}{\pi} \int_0^{\frac{\pi}{2}} dq \frac{\tanh(\frac{\beta_c}{2} |\mathcal{J}_0| \cos q)}{\mathcal{J}_0 \cos q} \left[(\gamma^2 \mathcal{J}_0^2 + \frac{1}{2} \mathcal{J}_1^2) \sin^2 q + |\mathcal{J}_1| (4 \gamma^2 \mathcal{J}_0^2 \cos^2 q + \gamma^2 \mathcal{J}_0^2 \sin^4 q + \right. \\ \left. + \frac{1}{4} \mathcal{J}_1^2 \sin^4 q)^{\frac{1}{2}} \right] = \omega_0. \quad (\text{III},33)$$

For $\mathcal{J}_1 = 0, \gamma \neq 0$ it reduces to

$$\frac{\gamma^2 \mathcal{J}_0^2}{2\pi} \int_0^{\frac{\pi}{2}} dq \frac{\tanh(\frac{\beta_c}{2} |\mathcal{J}_0| \cos q)}{\cos q} \sin^2 q = \omega_0, \quad (\text{III},34)$$

and for $\mathcal{J}_1 \neq 0, \gamma = 0$ it reduces to

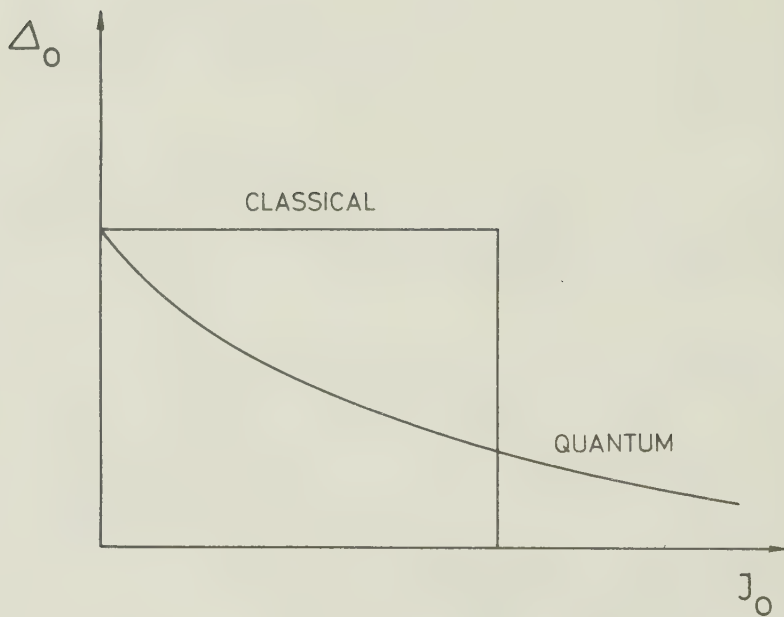


Fig. 12: $T = 0$ lattice distortion as a function of J_0 for classical and quantum spin systems (schematically)

$$\frac{1}{4} \frac{J_1^2}{J_0^2} \int_0^{\pi/2} dq \frac{\tanh\left(\frac{\beta_c}{2} |J_0| \cos q\right)}{\cos q} \sin^2 q = c c_c \quad (\text{III},35)$$

It is instructive to compare the solution of (III,35) with the solutions of the analogous Eq. (II,25) for the classical model. By expanding the integrand in (III,35) for small $|J_0|$ and computing the first two terms from the series, we obtain

$$T_c(x, J_0) = T_c(x, 0) - O(J_0^2) + \dots \quad (\text{III},36)$$

where, as before, $x = \frac{J_1^2}{\omega_0^2}$ and $T_c(x, 0) = \frac{J_1^2}{16\omega_0 k_B}$. We note that (III,36) is apart from a numerical factor, of the same form as the Eq. (II,25) for the classical n-vector model. In both cases J_0 decreases the critical temperature for the lattice distortion and the first term in the small J_0 expansion is quadratic in J_0 . A similar calculation for (III,33) can be done only numerically.

In order to check whether the transition described by (III,33) is of first or second order, it is necessary to investigate the fourth order term in Δ in the small Δ expansion of $f(\Delta, T)$. It turns out that for both cases $(J_1 \neq 0, \gamma = 0)$, $(J_1 = 0, \gamma \neq 0)$ a term $\sim \Delta^4$ is only weakly temperature-dependent and is positive for all values of J_0 . The transition at T_c is therefore of second order. Because of extreme complexity of the expansion coefficients of $f(\Delta, T)$ for $J_1 \neq 0, \gamma \neq 0$ we were not able to prove that the

transition is of second order, but we are strongly tempted to believe that this is the case.

5. CONCLUSIONS AND DISCUSSION

By considering the spin-Peierls transition in the alternating, anisotropic, spin 1/2 X-Y model coupled to a single mode of a harmonic lattice we have found that at $T = 0$ it is always energetically favorable to develop a periodic distortion on a linear chain. Furthermore, the transition is always of the second order. These two features are in a sharp contrast with the results of chapter II, where the classical spin models were shown to display first or second order transition depending on the value of J_0 . For large enough J_0 the classical chain is undistorted. The above differences originate from the truly quantum mechanical character of the X-Y model. The necessity of introducing the collective quasi-particle operators in the solution of X-Y model indicates that collective properties of it cause the second order transition.

In contrast, the n-vector model partition function being simply a product of bond partition functions does not reflect the collective character of the phase transition and this causes the first order transition.

Let us point out that the question of the spin long range order for the groundstate has yet to be solved even for the simpler case of anisotropic X-Y model without the coupling to the lattice⁽³⁰⁾.

It remains open also for our more complicated model system. The simple, energetical arguments applied to the classical model are not useful here due to the quantum nature of the problem.

The model Hamiltonian considered here (see Eq. (III,15)) bears a strong resemblance to the phenomenological approaches to the Peierls transition in electronic systems with the BCS type electron-electron interaction⁽²³⁾. Since we have been dealing with spinless fermions, there is no spin selection rule acting on our Hamiltonian and we had a larger number of non-vanishing matrix elements as in⁽²³⁾. We note, however, that the mathematical similarity between our theory and BCS⁽¹⁹⁾ as well as the mean field theory of the Peierls transition⁽²⁰⁾ is quite transparent.

Finally, we observe that for $J_0 = J_1 \Delta$ and $\gamma = C$ the free energy (III,27) goes over to that of the classical Ising model with $J_0 = 2J_1, J_1 = 0$. Such a peculiar "classical" limit will be considered in a forthcoming publication.⁽³³⁾

CHAPTER IV

PEIERLS TRANSITION IN DISPLACIVE FERROELECTRIC SYSTEMS.

1. INTRODUCTION

In previous Chapter we have investigated the collective Peierls and spin-Peierls transitions. They were caused by the electron-lattice and spin-lattice interactions respectively. The lattice distortions due to these interactions (which are linear in Δr_{ij}) have lowered the electronic (Peierls transition) and spin (spin-Peierls transition) energies which in turn had to be balanced against the positive elastic energies of distortion.

The electron- and spin-lattice interactions have arisen from the expansion of the interionic potential and the exchange integral respectively up to first order in the displacements Δr_{ij} of the ions from their equilibrium positions.

In this context it is of interest to ask how these lattice distortions relate to those occurring in ferro- and antiferroelectrics.

Ferro- and antiferroelectric materials are characterized by the existence of one or more asymmetric positions with respect to the unit cell. By lowering the temperature these positions start to be occupied by ions or groups of ions leading to the appearance of non-vanishing electric polarization with the accompanying lattice distortion. It is the purpose of this Chapter to study the mutual rela-

tionship of the two mechanisms leading to the appearance of the lattice distortion: the electron-lattice interaction and the ferroelectric lattice interaction.

Let us note in passing that the problem of the coexistence of superconductivity and ferroelectricity attracted a considerable attention ⁽⁶⁴⁾ some years ago. Since the mathematical structure of the theory of Peierls transition and the BCS theory of superconductivity is very similar, the problem of the interrelation between the Peierls and ferroelectric instabilities is particularly interesting. Moreover, there exist recent speculative attempts to interpret the structural transitions in (TTF-TCNQ) and in related compounds solely in terms of the ferroelectric instability ^(34,35).

It has become conventional now ⁽³⁶⁾ to classify the ferroelectrics according to the form of the local part of the potential which is experienced by the ions producing the electrical polarization. In the so called order-disorder ferroelectrics ⁽³⁷⁾ (best exemplified by KDP (KH_2PO_4)) there are usually two or more equilibrium positions in the unit cell which are equally populated at high temperatures. The local potential $V(\eta)$ (η is the distance from the center of unit cell) has therefore at least two minima at non-zero values of η , see Fig. 13a.

In the displacive ferroelectrics (for example BaTiO_3 ⁽³⁸⁾),

the local part of the potential possesses only one minimum at the center of the unit cell, see Fig. 13b. The non-zero minimum of the total potential which is needed for the non-zero polarization is brought about in the displacive case by the non-local part of the potential, whereas in order-disorder case it is already guaranteed by the local part of the potential. The non-local part of the potential (denoted here by $-\sum_{ij} J_{ij} \eta_i \eta_j$), with i and j referring to different cells) is attractive and usually of long range. It appears as a result of the interaction of the ions producing the polarization with all the ions of the same type in other cells.

In the following we will be concerned with the ferroelectric potentials of the displacive type.

It should be clearly emphasized that in the electron-lattice interaction even the terms linear in η_i can produce the collective lattice distortion. In the ferroelectric Hamiltonian $H_L = -\sum_{ij} J_{ij} \eta_i \eta_j + \sum_i V(\eta_i)$ one usually considers the terms which are at least quadratic in lattice coordinates η_i 's. The long range interaction J_{ij} is of electronic origin since it derives from the dipol-dipol interaction. In Section 5 we shall treat the electron-lattice system together with the ferroelectric system described by H_L . It should be kept in mind that such a division into electron-lattice and ferroelectric system is to some

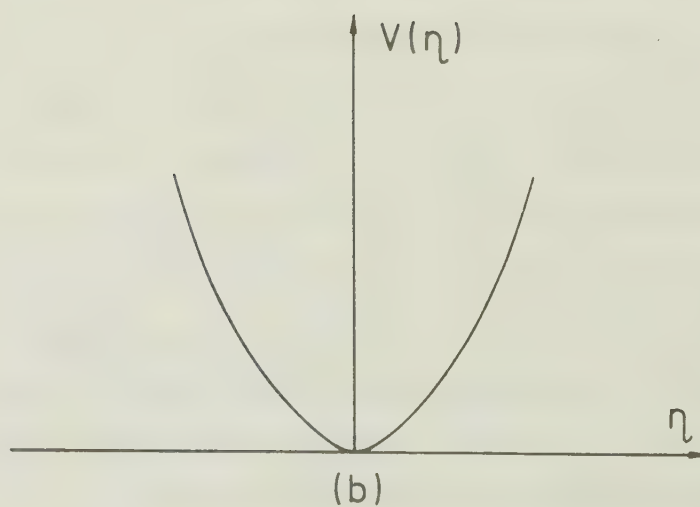
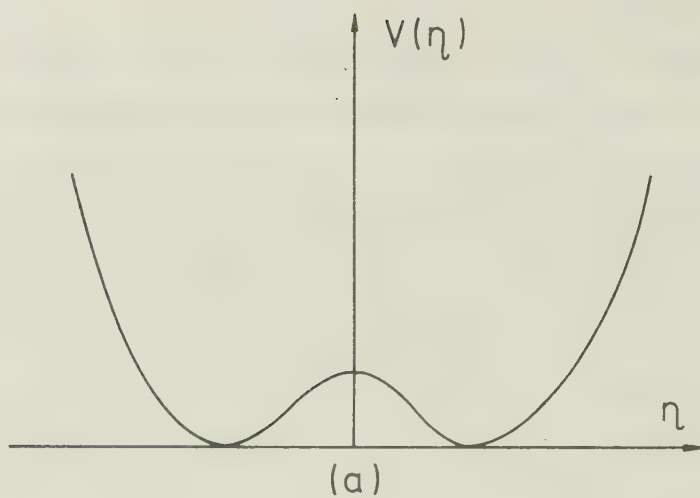


Fig. 13: Local parts of the lattice potential for the ferroelectrics of the order-disorder (a) and of the displacive type (b).

extend conventional since J_{ij} contains already the contributions from electron-lattice and electron-electron interactions as well.

Owing to the existence of the long range interactions the static properties of ferroelectrics are usually described by Landau-Devonshire phenomenological expansion of the free energy (39). We shall use a semimicroscopic Hamiltonian of Section 2 to derive explicitly the coefficients of the free energy expansion in Section 4 and 5.

In Section 2 we describe the Hamiltonian of the system. We consider the electron-lattice Hamiltonian, where also the ferroelectric lattice potential of displacive type is taken into account. The physical meaning of the terms of the Hamiltonian operator is discussed in detail.

In Section 3 we investigate within the mean field theory the condition the lattice potential must fulfill in order to produce the antiferroelectric distortion. We re-derive the known result that the anharmonicity is needed to produce the lattice distortion.

In Section 4 we present the self-consistent calculation of the temperature dependence of the lattice distortion, when the local quartic anharmonic terms in the lattice potential are included. The Landau expansion of the free energy is presented for the small anharmonicity case.

In Section 5 we present the mean field theory treatment of the temperature dependence of the antiferroelectric lattice distortion resulting from both the anharmonic lattice potential and the electron-lattice interaction. The expressions for the critical temperatures are derived and discussed for various values of the parameters involved. The combined effect of the quartic anharmonicity and the electron-lattice interaction for the producing the lattice distortion is analyzed.

In Section 6 we point out that in the absence of the electron-lattice interaction the mean field approach to the lattice potential makes it possible to investigate in a simple way the behaviour of the system displaying simultaneously antiferroelectric and ferroelectric distortion. The Landau expansion of the free energy in terms of the two above order parameters is presented. A possibility of ferro-antiferroelectric phase is considered.

Let us explain why we have focused our attention on displacive ferroelectrics. As it is well known the statistical mechanics of systems having a finite number of allowed states can be investigated using spin (or pseudo-spin) models. For instance, one describes the motion of ions in the order-disorder type of potential (Fig.13b) with the help of Ising type models ⁽³⁷⁾. The problem of the Peierls transition in order-disorder ferroelectrics would then approximately reduce to the Peierls transition in coupled electron

and pseudo-spin system, a problem treated in Chapter II.

2. HAMILTONIAN OF THE SYSTEM

Consider a linear chain of ions with the lattice spacing a . With every ion l we associate the coordinate η_l which describes the deviation of the ion from its equilibrium position. The neighboring ions interact with each other by means of the elastic potential energy

$$H_E = \frac{1}{2} k \sum_{\langle ij \rangle} (\eta_i - \eta_j)^2, \quad (IV,1)$$

where the summation is over nearest neighbors, and where k is the appropriate elastic constant. The kinetic energy associated with η_l has been neglected. The long range part of the interaction between ions is represented by the attractive two body force

$$V_L = -\frac{1}{2} \sum_{ij} J_{ij} \eta_i \eta_j, \quad i \neq j. \quad (IV,2)$$

In addition, every ion in the chain experiences a repulsive local potential $V'(\eta)$ due to all the other ions in the unit cell. The total lattice Hamiltonian $H_L = H_E + V_L + V'$ is

$$H_L = -\frac{1}{2} \sum_{ij} J_{ij} \eta_i \eta_j + \sum_i k \eta_i^2 + \sum_i V'(\eta_i),$$

where we have introduced the notation

$$J_{ij} = J_{ij} + K \delta_{i,j+1}$$

Denoting also $V(\eta_i) = k\eta_i^2 + V'(\eta_i)$ the lattice Hamiltonian reads

$$H_L = -\frac{1}{2} \sum_{ij} J_{ij} \eta_i \eta_j + \sum_i V(\eta_i). \quad (\text{IV}, 3)$$

We note that the total local potential $V(\eta_i)$ originates from the elastic energy as well as from the potential $V'(\eta_i)$ of all the other ions in the unit cell. We shall not specify the form of $V(\eta)$ as yet, we require only that $V(\eta) = V(-\eta)$. For the electrons interacting with the lattice we adopt the tight-binding Hamiltonian as in the Eq. (II,5):

$$H_e + H_{e-L} = \sum_{i\sigma} t_{i,i+1} (C_{i\sigma}^\dagger C_{i+1\sigma} + C_{i+1\sigma}^\dagger C_{i\sigma}) + \sum_{i\sigma} g_{i,i+1} (C_{i\sigma}^\dagger C_{i+1\sigma} + C_{i+1\sigma}^\dagger C_{i\sigma}) \cdot (\eta_{i+1} - \eta_i), \quad (\text{IV}, 4)$$

where $t_{i,i+1}$ is the hopping integral and $g_{i,i+1}$ is the electron-lattice coupling constant. The total Hamiltonian operator of the system will be

$$H = H_L + H_e + H_{e-L}. \quad (\text{IV}, 4)$$

We should be aware of the fact that the simple tight-binding Hamiltonian linear in η_i 's can be also seen to ob-

tain higher order anharmonic effects as well. Quite formally, one could approximately write down the free energy associated with (IV,4) and perform the Taylor expansion for small lattice distortion. One would then end up with an expression similar to (IV,25), which describes the fourth order anharmonicity effects. By allowing a general form (IV,3) for the lattice part H_L of the Hamiltonian we have generalized the simpler form of the H_L of Chapter II to include explicitly the non-local part J_{ij} (which includes the elastic part) and a general local part $V(\eta)$. It is not possible to solve the Hamiltonian (IV,4) exactly. In the next two sections we shall resort to the mean field approximation in treating H_L for the case $g = 0$.

3. ROLE OF LATTICE ANHARMONICITY IN PRODUCING THE ANTIFERRO-ELECTRIC LATTICE DISTORTION ($g = 0$).

In order to investigate the condition under which a non zero $\langle \eta_i \rangle$ can appear we shall make use of the identity

$$\eta_i = \langle \eta_i \rangle + (\eta_i - \langle \eta_i \rangle) \quad (\text{IV}, 5)$$

by substituting it back to the Eq. (IV,3). Then the Hamiltonian H_L takes on the following form:

$$H_L \equiv \frac{1}{2} \sum_{i \neq j} J_{ij} \langle \eta_i \rangle \langle \eta_j \rangle - \sum_i \eta_i \sum_j J_{ij} \langle \eta_j \rangle - \frac{1}{2} \sum_{i \neq j} J_{ij} (\eta_i - \langle \eta_i \rangle) (\eta_j - \langle \eta_j \rangle) + \sum_i V(\eta_i). \quad (\text{IV}, 6)$$

The mean field approximation (MFA) applied then to Eq. (IV,6)

consists now in neglecting the term $-\sum_{i \neq j} J_{ij} (\eta_i - \langle \eta_i \rangle) \times (\eta_j - \langle \eta_j \rangle)$ which is quadratic in the fluctuations

$\eta_i - \langle \eta_i \rangle$, which were assumed to be small. By Fourier transforming (IV,6) we obtain

$$H_L = \frac{1}{2} \sum_q J(q) \langle \eta_q \rangle \langle \eta_q \rangle - \sum_{iq} \eta_i J(q) \langle \eta_q \rangle e^{iq \cdot R_i} + \sum_i V(\eta_i). \quad (\text{IV}, 7)$$

Since we are interested in the antiferroelectric distortion we single out from the q summation in (IV,7) only one q term with $q = \frac{\pi}{a}$. The lattice Hamiltonian reads then

$$H_L = \frac{N}{2} J_{\pi} \delta^2 - \sum_l J_{\pi} \eta_l \delta e^{i \frac{\pi}{a} l a} + \sum_l V(\eta_l) = \frac{N}{2} J_{\pi} \delta^2 - \sum_l J_{\pi} \eta_l \delta (-1)^l + \sum_l V(\eta_l), \quad (\text{IV}, 8)$$

where

$$J\left(\frac{\pi}{a}\right) = J_{\pi}, \quad \langle \eta_{\frac{\pi}{a}} \rangle = \langle \eta_{\frac{\pi}{a}} \rangle \equiv \delta.$$

δ describes the antiferroelectric order parameter whose sign alternates from cell to cell. H_L can be rewritten as a sum of single cell Hamiltonians H_L

$$H_L = \sum_l H_l, \quad (IV,9)$$

where

$$H_l = \frac{J_\pi}{2} \delta^2 - J_\pi \eta_l \delta (-1)^l + V(\eta_l). \quad (IV,10)$$

The free energy per cell resulting from (IV,9) is then

$$f(\delta, T) = \frac{J_\pi}{2} \delta^2 - \frac{1}{\beta} \ln \int_{-\infty}^{\infty} d\eta \exp[-\beta(V(\eta) - J_\pi \eta \delta)]. \quad (IV,11)$$

In deriving Eq. (IV,11) we took into account that the variable η is describable by the classical statistics; furthermore, since $V(\eta)$ was assumed symmetric the change of sign $(-1)^l$ in the second term of (IV,10) does not change the value of the integral in (IV,11) since it corresponds to the change of variables $\eta \rightarrow -\eta$. The equilibrium value of the order parameter δ can be obtained from the minimization of the free energy, $\partial f / \partial \delta = 0$. Thus, one finds

$$\delta = \frac{\int_{-\infty}^{\infty} d\eta \eta \exp[-\beta(V(\eta) - J_\pi \eta \delta)]}{\int_{-\infty}^{\infty} d\eta \exp[-\beta(V(\eta) - J_\pi \eta \delta)]}. \quad (IV,12)$$

By solving (IV,12) for δ at any given temperature one obtains $\delta = \delta(T)$. Since we are interested in the behaviour of δ near its transition temperature we shall rather use the closed form expression for the free energy (IV,11) and expand it for small δ . It is easy to check that $f(\delta, T) = f(-\delta, T)$

and therefore only the even terms in δ enter the small δ expansion of f . One obtains

$$f(\delta, T) = \left[\frac{J_\pi}{2} - \frac{a'(T)}{2} \right] \delta^2 + \frac{b'(T)}{4!} \delta^4 + \dots \quad (\text{IV}, 13)$$

where

$$a'(T) = \beta J_0^2 \langle \eta^2 \rangle_{\delta=0} \quad (\text{IV}, 14a)$$

and

$$b'(T) = \beta^3 J_0^4 (3 \langle \eta^4 \rangle - \langle \eta^2 \rangle^2)_{\delta=0} \quad (\text{IV}, 14b)$$

with

$$\langle \eta^k \rangle = \frac{\int_{-\infty}^{\infty} d\eta \eta^k \exp[-\beta(V(\eta) - J_\pi \eta \delta)]}{\int_{-\infty}^{\infty} d\eta \exp[-\beta(V(\eta) - J_\pi \eta \delta)]} \quad (\text{IV}, 15)$$

In the spirit of the Landau theory of phase transitions the transition temperature for δ is determined by the vanishing of the second order term in δ in (IV,13). In order to calculate the averages (IV,14) the explicit form of the potential $V(\eta)$ is needed. It is however easy to convince oneself that for the simplest allowed form of $V(\eta)$: $V(\eta) = \frac{1}{2} V_2 \eta^2$ the second order term in (IV,13) does not show any temperature dependence, therefore excluding any transition as the function of temperature.

We have thus rederived the long known fact that the classical harmonic lattice does not show any temperature effects (8).

In order to obtain a non-zero value of the order parameter δ one must include higher order terms in the lattice potential $V(\eta)$. The simplest form of the symmetric, anharmonic, displacive type local potential which will be sub-

sequently used is

$$V(\eta) = \frac{1}{2} V_2 \eta^2 + \frac{1}{4} V_4 \eta^4, \quad V_2 > 0, V_4 > 0. \quad (\text{IV}, 15)$$

It is interesting to note, that the equation for the transition temperature of δ (within the mean field approximation for J_{ij}) can be written down for arbitrary V_4 in terms of the known functions. For the mathematical details we refer to the Appendix E. The implicit equation for $\beta_c = \frac{1}{k_B T_c}$ is (see Eqs. (E,3) and (E,7))

$$\left(\frac{1}{\beta_c} \right)^{\frac{1}{2}} \left(\frac{V_4}{3^{\frac{1}{2}} \Gamma} \right)^{\frac{1}{2}} = \frac{D_{-\frac{1}{2}} \left[\left(\frac{\beta_c V_2}{2 V_4} \right)^{\frac{1}{2}} \right]}{D_{-\frac{3}{2}} \left[\left(\frac{\beta_c V_2}{2 V_4} \right)^{\frac{1}{2}} \right]}, \quad (\text{IV}, 16)$$

where $D_\nu(z)$ is the parabolic cylinder function of order ν (40). The analytical solution of (IV,16) for different values of parameters involved is not an easy task, due to the complicated form of appropriate asymptotic expansions of $D_\nu(z)$.

We shall rather treat the physically important case of small anharmonicity V_4 , which can be also performed analytically. The calculations can be done directly by using the free energy expression (IV,11) specified for small V_4

In this case

$$\begin{aligned} \psi(\beta, T) &= \frac{\Gamma_\pi}{2} \delta^2 - \frac{1}{\beta} \ln \int_{-\infty}^{\infty} d\eta \exp \left[-\beta \left(\frac{V_2}{2} \eta^2 + \frac{V_4}{4} \eta^4 - \Gamma_\pi \eta \delta \right) \right] = \\ &\approx \frac{\Gamma_\pi}{2} \delta^2 - \frac{1}{\beta} \ln \int_{-\infty}^{\infty} d\eta \exp \left[-\beta \left(\frac{V_2}{2} \eta^2 - \Gamma_\pi \eta \delta \right) \right] \left(1 - \frac{\beta V_4}{4} \eta^4 \right). \end{aligned} \quad (\text{IV}, 17)$$

Expanding also the logarithm in (IV,17) we end up with

$$f(\delta, T) = \frac{J\pi}{2} \delta^2 - \left\{ \frac{1}{\beta} \ln \int_{-\infty}^{\infty} d\eta \exp \left[-\beta \left(\frac{V_2}{2} \eta^2 - J\pi \eta \delta \right) \right] \right\} + \frac{V_4}{4} \frac{\int_{-\infty}^{\infty} d\eta \eta^4 \exp \left[-\beta \left(\frac{V_2}{2} \eta^2 - J\pi \eta \delta \right) \right]}{\int_{-\infty}^{\infty} d\eta \exp \left[-\beta \left(\frac{V_2}{2} \eta^2 - J\pi \eta \delta \right) \right]} \quad (1)$$

We shall use this last form of $f(\delta, T)$ in the next Section for performing its small δ expansion.

4. THE LANDAU EXPANSION OF THE FREE ENERGY FOR THE CASE OF SMALL ANHARMONICITY.

The self-consistency equation for δ resulting from $\frac{\partial f}{\partial \delta} = 0$ with $f(\delta, T)$ approximated by Eq. (IV,18) can be cast in the form

$$\delta = \delta_0 + \frac{\beta V_4}{4} (\langle \eta^5 \rangle_0 - \delta_0 \langle \eta^4 \rangle_0) ,$$

where the quantities with the subscript "zero" denote the averages with $V_4 = 0$ — in other words the averages which were performed in the previous section. The critical temperature is obtained as usual from the requirement that the second derivative of the free energy taken at $\delta = 0$ vanishes. Within the approximation (IV,18) one obtains for

this derivative

$$\begin{aligned} \frac{\partial^2 f(\delta, T)}{\partial \delta^2} \Big|_{\delta=0} &= J_{\pi} - J_{\pi} \beta (\langle \eta^2 \rangle_0 - (\langle \eta \rangle_0)^2) \Big|_{\delta=0} + \\ &+ \frac{V_4 \beta^4 J_{\pi}^2}{4} (\langle \eta^6 \rangle_0 - \langle \eta^2 \rangle_0 \langle \eta^4 \rangle_0) \Big|_{\delta=0} = \\ &= J_{\pi} - J_{\pi} \beta \langle \eta^2 \rangle_0 \Big|_{\delta=0} + \frac{V_4 \beta^4 J_{\pi}^2}{4} (\langle \eta^6 \rangle_0 - \langle \eta^2 \rangle_0 \langle \eta^4 \rangle_0) \Big|_{\delta=0} \end{aligned} \quad (IV, 19)$$

The averages in (IV,19) can be easily calculated since they

all reduce to the integrals of the type $\int x^n e^{-\alpha x^2} dx$;

they are equal: $\langle \eta^2 \rangle_0 = (\beta V_2)^{-1}$, $\langle \eta^4 \rangle_0 = (3\beta^3 V_2^2)^{-1}$ and

$\langle \eta^6 \rangle_0 = 15(\beta^3 V_2^3)^{-1}$, where δ was set to zero.

By substituting them to the equation for T_c

$$\frac{\partial^2 f(\delta, T_c)}{\partial \delta^2} \Big|_{\delta=0} = J_{\pi} \left(1 - \frac{J_{\pi}}{V_2} + \frac{3J_{\pi} V_4 k_B T_c}{V_2^3} \right), \quad (IV, 20)$$

or, equivalently,

$$T_c = T_c(J, V_2, V_4) = \frac{V_2^2}{3V_4 k_B} \frac{J_{\pi} - V_2}{J_{\pi}}, \quad (V_4 \neq 0). \quad (IV, 21)$$

To ensure that the critical temperature obtained this way

corresponds to the second order phase transition we must

check, whether the next higher order term in the δ expansion

(in this case $\sim \delta^4$) remains positive at T_c . The third

derivative of f is then

$$\begin{aligned} \frac{\partial^3 f}{\partial \delta^3} \Big|_{\delta \neq 0} &= -\beta^3 J_{\pi}^3 [\langle \eta^3 \rangle_0 - 3\langle \eta \rangle_0 \langle \eta^2 \rangle_0 + 2(\langle \eta \rangle_0)^3] + \\ &+ \frac{V_4 \beta^3 J_{\pi}^3}{4} [\langle \eta^7 \rangle_0 - 3\langle \eta \rangle_0 \langle \eta^6 \rangle_0 + 6\langle \eta^5 \rangle_0 \langle \eta \rangle_0^2 + 6\langle \eta^4 \rangle_0 \langle \eta^2 \rangle_0 \langle \eta \rangle_0 + \\ &- 3\langle \eta^5 \rangle_0 \langle \eta^2 \rangle_0 - 6\langle \eta^4 \rangle_0 (\langle \eta \rangle_0)^3 - \langle \eta^4 \rangle_0 \langle \eta^3 \rangle_0]. \end{aligned} \quad (IV, 22)$$

By differentiating the above expression once again with respect to δ and setting $\delta \rightarrow 0$ (only even order averages do not vanish!) the following expression for $\left. \frac{\partial^4 \phi}{\partial \delta^4} \right|_{\delta=0}$ results

$$\left. \frac{\partial^4 \phi}{\partial \delta^4} \right|_{\delta=0} = -\beta^3 J_{\pi}^4 \left[\langle \eta^4 \rangle_0 - 3(\langle \eta^2 \rangle_0)^2 \right] + \frac{V_4 \beta^4 J_{\pi}^4}{4} \left[\langle \eta^8 \rangle_0 - 6\langle \eta^6 \rangle_0 \langle \eta^2 \rangle_0 + 6\langle \eta^4 \rangle_0 (\langle \eta^2 \rangle_0)^2 - (\langle \eta^4 \rangle_0)^2 \right]. \quad (\text{IV}, 28)$$

Using $\langle \eta^8 \rangle_0 = \frac{105}{\beta^4 V_2^4}$ and for other averages the results previously quoted one ends up with

$$\left. \frac{\partial^4 \phi}{\partial \delta^4} \right|_{\delta=0} = \frac{6V_4 J_{\pi}^4}{V_2^4}. \quad (\text{IV}, 29)$$

The complete Landau expansion of the free energy for small V_4 is then

$$\phi(\delta, T) = a \cdot (T - T_c) \delta^2 + b \delta^4 + \dots \quad (\text{IV}, 29)$$

with

$$a = \frac{3}{2} \frac{J_{\pi}^2 V_4 k_B}{V_2^3}, \quad T_c = \frac{V_2^2}{3V_4 k_B} \frac{J_{\pi} - V_2}{V_2}, \quad b = \frac{1}{4} \frac{V_4 J_{\pi}^4}{V_2^4} \quad (\text{IV}, 29)$$

Since $b > 0$ and is temperature independent the critical temperature T_c describes the second order phase transition.

The approximate expressions (IV,25) and (IV,26) reflect semiquantitatively the necessary conditions which should be imposed on the parameters of the Hamiltonian in order to produce the phase transition.

First of all - a non-vanishing anharmonicity is required. By increasing the anharmonicity one makes the local potential steeper. Therefore, it is more difficult to produce the lattice distortion and effectively the transition temperature is lowered. Furthermore, in order to obtain a positive critical temperature, the long range two body interaction J should be always larger than the harmonic part of the local potential V_2 . (In real physical crystals the anharmonicity V_4 is much smaller than $V_2 a^2$). In order that the critical temperature be of the order of hundreds degrees $^{\circ}\text{K}$ one must assume that $J_{\pi} \gtrsim V_2$; so it is larger, but it almost compensates V_2 .

One can supply another argument justifying the expressions (IV,26) for the coefficients of Landau expansion and for the transition temperature. We consider Eq. (IV,3) at $T = 0$. The free energy should be minimum with respect to all η_i 's. From this condition we obtain

$$(\eta_i^2)_{T=0} = \delta^2(T=0) = \frac{J_{\pi} - V_2}{V_4} ,$$

which again shows the necessity of $J_{\pi} > V_2$.

It is interesting to compare the roles of V_2 and V_4 in producing the finite transition temperature in (IV,26): for $V_2 \rightarrow 0$ T_c vanishes, since V_2 is needed to stabilize the system against the long range attraction J_{ij} . By increasing V_2 initially increases and then for $\frac{2}{3}J_\pi < V_2 < J_\pi$ decreases and reaches zero for $J_\pi = V_2$. Similarly, by increasing V_4 (for small V_4) T_c decreases. By increasing V_2 and V_4 the local potential becomes steeper and it becomes more difficult for an ion to move to some $\eta \neq 0$ position. In other words, the critical temperature for the distortion decreases.

We believe that the improvement of the mean field approximation and a more accurate treatment of the anharmonicity will not change these results significantly.

In the next Section we are going to analyze how the inclusion of yet another mechanism producing the lattice distortion, namely the electron-phonon interaction, will affect the results obtained before.

5. TEMPERATURE DEPENDENCE OF THE ANTIFERROELECTRIC LATTICE DISTORTION IN THE PRESENCE OF THE ELECTRON-LATTICE INTERACTION

In this Section we shall present the calculations of the temperature dependence of δ resulting from the full Hamiltonian with the electron-lattice interaction (IV,4). The free

energy of the system is a sum of the free energies corresponding to H_L and to $H_e + H_{e-L}$. While the free energy of H_L has been derived in the previous Section, we shall follow exactly the steps outlined in Section 3 of Chapter II, to write down the free energy of $H_e + H_{e-L}$.

In writing $H_e + H_{e-L}$ in the momentum space, we shall single out from all the q -summations only the term associated with $q = \frac{\pi}{a}$ which is equal to $2k_F$ for a half filled electronic band. We define the order parameter δ associated with the distortion of the l -th ions by

$$g(2k_F) \eta_{2k_F} e^{i2k_F R_0^l} \equiv g \cdot \delta (-1)^l. \quad (IV, 27)$$

With the constraint (IV, 27) the electron-lattice Hamiltonian can be then diagonalized⁽⁹⁾ and the total free energy takes on the following form

$$\begin{aligned} F/N &= \mathcal{F} = \mathcal{F}_L + \mathcal{F}_{e-L} = \\ &= \frac{\mathcal{J}}{2} \delta^2 - \frac{1}{\beta} \ln \int_{-\infty}^{\infty} d\eta \exp \left[-\beta \left(\frac{V_2}{2} \eta^2 + \frac{V_1}{4} \eta - \mathcal{J} \eta \delta \right) \right] \\ &\quad - \frac{1}{\beta} \int d\epsilon N(\epsilon) \ln \left[2 \cosh \frac{\beta}{2} \sqrt{\epsilon^2 + (g\delta)^2} \right], \end{aligned} \quad (IV, 28)$$

where the subscript π on $\mathcal{J}$ was dropped for simplicity, and $N(\epsilon)$ is the electronic density of states in the band.

The appearance of the lattice distortion is due to the

competition of J_{ij} and V on one hand and to the electron-lattice interaction g on the other hand. Within the approximations which have led to (IV,28) these two mechanisms are independent.

We shall attempt now to find out what is the effect of these two mechanisms on the overall transition temperature and, in particular, how the necessary conditions for the appearance of the lattice distortion discussed in the previous Section would be altered, if the electron-lattice interaction is switched on.

First of all, by setting $\frac{\partial \mathcal{F}}{\partial \delta} = 0$ we obtain the following self-consistency equation for $\delta = \delta(T)$:

$$J \left(\delta - \frac{\int_{-\infty}^{\infty} d\eta \eta \exp[-\beta(V(\eta) - J\eta\delta)]}{\int_{-\infty}^{\infty} d\eta \exp[-\beta(V(\eta) - J\eta\delta)]} \right) = \delta g^2 \int d\epsilon N(\epsilon) \frac{\tanh \frac{\beta}{2} \sqrt{\epsilon^2 + (g\delta)^2}}{2\sqrt{\epsilon^2 + (g\delta)^2}} \quad (\text{IV},29)$$

We observe that the right-hand side of Eq. (IV,29) is always positive.

In order to find the over-all transition temperature, we differentiate (IV,29) once again with respect to δ and set $\delta=0$. This way the following equation for T_p is obtained

$$J(1-\beta_F) \langle \eta^2 \rangle \Big|_{\epsilon=0} = g^2 N(0) \int_0^{\epsilon_F} d\epsilon \frac{\tanh \frac{\beta_F \epsilon}{2}}{\epsilon} . \quad (IV,30)$$

We can easily check that (IV,30) possesses a finite solution even for $V_4=0$. For this case $\langle \eta^2 \rangle = (\beta V_2)^{-1}$ and (IV,30) can be solved to give

$$T_p \approx 1.14 \epsilon_F \exp \left[- \frac{1}{\frac{g^2 N(0)}{J_{eff}}} \right] \quad (IV,31)$$

with

$$J_{eff} = J \left(1 - \frac{J}{V_2} \right) > 0 \quad (IV,32)$$

Since J_{eff} must be larger than zero, the condition for it is $V_2 > J$ which is just opposite to the condition (IV,26). This result can be interpreted as an indication that the electron-lattice interaction effectively produces a very strong anharmonic lattice potential which produces the critical temperature (IV,31). On the other hand, for $V_4=0$ the harmonic lattice can be treated exactly and therefore the results (IV,30) - (IV,32) should be viewed as an artifact of the mean field approximation applied to the exactly soluble system.

For $V_4 \neq 0$, and small, this approximation becomes meaningful and we are going to exploit it in the further analysis of (IV,28).

The equation for the critical temperature T_c in the presence of small V_4 using (IV,20) becomes

$$J(1 - \frac{J}{V_2} + \frac{3J^2 V_4 k_B T_c}{V_2^3}) - g^2 N(0) \int_0^{\epsilon_F} d\epsilon \frac{\tanh \frac{\beta_0 \epsilon}{2}}{\epsilon} = 0 \quad (IV,32)$$

which using Eq. (IV,31) can be rewritten as

$$-g^2 N(0) \ln \frac{T_p(J_{eff})}{T_0} + \frac{3J^2 V_4 k_B T_0}{V_2^3} = 0 \quad (IV,33)$$

(This last form is strictly valid only for $T_p(J_{eff}) \approx T_0$)

For $g=0$ in (IV,32) (in the absence of linear in η terms in the Hamiltonian) we obtain again the results of the previous section.

Eq. (IV,32) can now be transformed into

$$g^2 N(0) \ln T_p(J_{eff}) = g^2 N(0) \ln T_0 + \frac{3J^2 V_4 k_B T_0}{V_2^3}, (g \neq 0). \quad (IV,34)$$

It is clear from (IV,32) that the increasing of V_4 (V_4 small) causes the decrease of T_0 in analogy to the Eq. (IV,21). However, due to the logarithmic term in (IV,34) this decrease is slower than for $g=0$. One can then conclude that the small an-

harmonicity V_4 lowers the transition temperature for the lattice distortion. The presence of the electron-lattice interaction weakens this effect. Since the above results were obtained in small V_4 approximation one cannot safely draw any conclusions regarding the values of V_4 for which the critical temperature would be driven to zero.

6. A POSSIBILITY OF COUPLED FERROELECTRIC AND ANTIFERROELECTRIC DISTORTIONS

In addition to alternating from site to site antiferroelectric distortion one can envisage more complicated lattice deformations which could be produced by the interactions of Hamiltonian (N_3). Perhaps the simplest example of interest is a deformation depicted in Fig. 14. It can be described as combined $q = 0$ and $q = \frac{\pi}{a}$ distortion. One can also imagine a deformation with a combination of more values of q . The method developed in Section 3 allows for the inclusion of several q values in the analysis of distortion.

In this Section we are going to demonstrate that the inclusion of $q = \frac{\pi}{a}$ and $q = 0$ components provides us a simple example of the mean field theory with coupled antiferroelectric ($q = \frac{\pi}{a}$) and ferroelectric ($q = 0$) order parameters. Interesting conclusions about the existence of a "mixed" phase (Fig. 14) will be drawn.

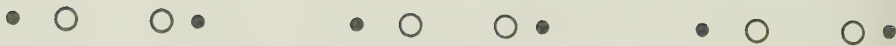


Fig. 14: A mixed state of combined ferro- and antiferroelectric distortions.

Consider once again the Eq. (IV,7),

$$H_L = \frac{1}{2} \sum_q J(q) \langle \eta_q \rangle \langle \eta_{-q} \rangle - \sum_i \eta_i J(q) \langle \eta_q \rangle e^{iqR_i^0} + \sum_i V(\eta_i). \quad (IV,7)$$

Let us single out from the q summation two values of q : $q = \frac{\pi}{a}$ corresponding to the antiferroelectric distortion and $q=0$ describing the ferroelectric (uniform) distortion. If we denote $\langle \eta_{\frac{\pi}{a}} \rangle = \delta$, $\langle \eta_0 \rangle = \epsilon$, $J(\frac{\pi}{a}) = J$, $J(0) = J'$ then we obtain from (IV,7)

$$H_L' = \frac{N}{2} J \delta^2 + \frac{N}{2} J' \epsilon^2 - \sum_i \eta_i [J(-1)^i \delta + J' \epsilon] + \sum_i V(\eta_i). \quad (IV,35)$$

In full analogy to (IV,11) the free energy per cell associated with H_L' can be readily written down and is equal

$$\psi = \frac{1}{2} (J \delta^2 + J' \epsilon^2) - \frac{1}{\beta} \ln \int d\eta \exp[-\beta(V(\eta) - J\eta\delta - J'\eta\epsilon)] \cosh(\beta J \eta \delta). \quad (IV,36)$$

The factor $\cosh(\beta J \eta \delta)$ arises because once we have fixed the sign of the ferroelectric order parameter ϵ throughout the chain, we will have according to (IV,35), $\frac{1}{2}N$ cells with $J\delta + J'\epsilon$ and $\frac{1}{2}N$ cells with $-J\delta + J'\epsilon$. By computing the free energy per cell this is explicitly taken care of by $\cosh(\beta J \eta \delta)$ in (IV,36).

Given $\psi(\delta, \epsilon, T)$ the selfconsistency equations for $\delta(T)$ and $\epsilon(T)$

are given by $\frac{\partial \phi}{\partial \delta} = 0, \frac{\partial \phi}{\partial \epsilon} = 0$. We are now going to find the temperature dependence of $\delta(T)$ and $\epsilon(T)$ by performing the Landau expansion of $\phi(\delta, \epsilon, T)$ for both values of δ and ϵ small. As in Section 4, it can be done analytically only in the case of small anharmonicity V_4 . Calculations are done along the path indicated in Section 4.

After some algebra we obtain the following form of the Landau expansion

$$\phi = a_a(T - T_{ca})\delta^2 + b_a\delta^4 + a_f(T - T_{cf})\epsilon^2 + b_f\epsilon^4 + c\delta^2\epsilon^2 + \dots \quad (\text{IV}, 37)$$

where

$$a_a = \frac{3}{2} \frac{J V_4 k_B}{V_2^3}, \quad T_{ca} = \frac{V_2^2}{3 V_4 k_B} \frac{J - V_2}{V_2}, \quad b_a = \frac{1}{4} \frac{V_4 J^4}{V_2^4}, \quad (\text{IV}, 38)$$

$$a_f = \frac{3}{2} \frac{J' V_4 k_B}{V_2^3}, \quad T_{cf} = \frac{V_2^2}{3 V_4 k_B} \frac{J' - V_2}{V_2}, \quad b_f = \frac{1}{4} \frac{V_4 J'^4}{V_2^4}, \quad (\text{IV}, 39)$$

and

$$c = \frac{3}{2} \frac{V_4}{V_2^4} J^2 J'^2. \quad (\text{IV}, 40)$$

We observe that the order parameters δ and ϵ appear in a symmetrical way in ϕ . They are coupled through a biquadratic term

$c\delta^2\epsilon^2$ with $c > 0$. The term $\sim c$ favors the existence of a phase with both $\delta \neq 0$ and $\epsilon \neq 0$.

The coefficients in Eqs. (IV,38) and (IV,39) were derived from a semimicroscopic Hamiltonian H_L .

There exist a number of theoretical approaches aimed at the analysis of systems with coupled order parameters^(61,62). Most of them use the expansion of the type of (IV,35) with the coefficients treated as phenomenological constants. One sees that without the coupling term $c\delta^2\epsilon^2$ both δ and ϵ undergo second order phase transitions at T_{ca} and T_{cf} respectively. An important conclusion which can be drawn from the results of⁽⁶²⁾ is that the c term may induce a first order phase transition between δ -ordered (antiferroelectric) and ϵ -ordered (ferroelectric) phases. Using (IV,37 - 40) one sees that $c^2 > 4b_a b_f$ which in the notation of⁽⁶²⁾ corresponds to the strong coupling regime. The detailed analysis of (IV,35) predicts for $c^2 > 4b_a b_f$ a first order phase transition at $T_c' = T_c'(T_{ca}, T_{cf})$ between antiferro- and ferroelectric phases. We note that the existence and stability of a mixed antiferro-ferroelectric phase (Fig.14) would require $c^2 < 4b_a b_f$, an inequality which is not fulfilled by (IV,35). We feel, however, that the existence of such a mixed phase is not ruled out by our treatment, since the condition $c^2 < 4b_a b_f$ could be, for example, satisfied, if V_4 could be treated in higher than first order approximation.

Chapter V

RENORMALIZATION OF CRITICAL EXPONENTS

IN THE COMPRESSIBLE ISING MODEL *)

*) Major portions of this Chapter have been reported in Phys. Rev. B8, 2119 (1973).

1. INTRODUCTION

We shall be concerned in this Chapter with the critical behavior of a certain theoretical model describing a compressible magnetic system.⁽⁴²⁾ Although the phase transitions displayed by the models in which the spins are situated on a rigid lattice are rather far from being completely understood, the introduction of the coupling between magnetic and elastic degrees of freedom brings about new effects and new complications. The coupling between a system of interacting spins and interacting ions comes about mainly because the exchange interaction $J(\vec{r}_i, \vec{r}_j)$ between the spins associated with ions at $\vec{r}_i$ and $\vec{r}_j$ is a function of a distance $\vec{r}_i - \vec{r}_j$ between the ions.

There were several attempts in the past to introduce the elasticity to otherwise rigid magnetic models.^(43, 44, 45) All of them were based on the approximations which were difficult to justify, especially in the critical region. For example, a simplifying assumption that the exchange integral does not depend on instantaneous distance between the ions carrying spins but rather on an average volume of the system leads to a drastic conclusion that the transition is always of first order.⁽⁴⁴⁾ This does not agree with experiment: second order transitions do exist in compressible magnetic systems⁽⁴⁶⁾ and should be predicted by the theory.

However, the inclusion of realistic forces (in lattice part of the Hamiltonian and in $J(\vec{r}_i - \vec{r}_j)$) gives rise to the appearance of "effective"^(47, 48, 49, 50, 51) spin Hamiltonian which, in addition to usual 2-spin Ising interaction, contains a long range 4-spin⁽⁵¹⁾ interaction. In other words, realistic forces induce "elastic"⁽⁴⁸⁾

many-spin interactions which render the problem insoluble in a closed form. One can give arguments that within a certain approximation (droplet model^(51,53)), all the derivatives of the free energy of such a system remain finite at the critical point. Therefore, the long range interactions substantially change the overall picture of the phase transition as compared to the initial rigid magnetic system. Baker and Essam⁽¹¹⁾ (hereafter referred to as BE) invented a compressible magnetic model in which the elastic degrees of freedom can be "integrated away"; its classical Statistical Mechanics is equivalent to that of a rigid Ising model in which the exchange integral depends on external forces. The price which had to be paid for that is the absence of shear forces in the system and, subsequently, lack of spherical symmetry. No "effective" long range forces appear in this model. It also satisfies the requirements of Fisher⁽⁵⁴⁾ theory of renormalization of critical exponents (see also the ref. 58). Gunther, Bergman, and Imry⁽⁵⁵⁾ (subsequently denoted by GBI) solved the BE model in d-dimensions in λ -ensemble (to be described below), particularly suitable for studying phase transitions in contact with Fisher's theory.

In Section 2 we briefly sketch Fisher's assumption for the renormalization of exponents to occur and we outline the GBI results on Baker-Essam model. We find that the BE model complies explicitly with the assumptions of Fisher's theory.

In Section 3 we apply the Fisher's theory to find an expression for the temperature range around T_c , where the renormalization of exponents "sets in". The real system (in a sense of Fisher) is the compressible BE system, the ideal system is described by a rigid Ising model.

In Section 4 we discuss the results obtained in connection with the experimental situation.

It is interesting to point out that the BE model has inherent 1-d features as far as the lattice variables are concerned. This fact is connected with the particular choice of distance dependent terms in the Hamiltonian. The BE model was shown to be equivalent to a set of commuting 1-d spin-lattice Hamiltonians ⁽⁴¹⁾

$$H = \sum_{n=1}^{N-1} \left[\frac{p_n^2}{2m} + (a - b\zeta_n\zeta_{n+1})(u_{n+1} - u_n) + c(u_{n+1} - u_n)^2 \right] + \frac{p_N^2}{2m}.$$

The BE model is then directly related to the spin-lattice systems of Chapters II and III.

2. RELATION BETWEEN BE MODEL AND THEORY OF RENORMALIZATION OF EXPONENTS

Fisher supposes (I) that the ideal system with the free energy $F_0(T)$ ($h = 0$) has an infinite specific heat anomaly at $T = T_c^0$, i.e. $\alpha, \alpha' > 0$. For instance, the ideal entropy

$$S_0(T) = - \frac{\partial F_0}{\partial T} = S_c^0 + A(\Delta T)^{1-\alpha} + B\Delta T + \dots \quad (\text{Y1})$$

where $\Delta T = T - T_c^0$, $A, B > 0$.

The real system is derived from the ideal one by introducing a new pair of thermodynamically conjugated variables entering the Hamiltonian in the form $\lambda \int a(\vec{r}) d\vec{r}$; λ is the force and $a(\vec{r})$ the corresponding density.

It is further assumed (II) that the nature of transition remains ideal if observed at fixed λ . It can be shown that it just means that the free energy of the real system can be written in terms of the ideal free energy F_0 as

$$F = F(T, \lambda) = F_0[T^*(T, \lambda)] + g(T, \lambda), \quad (\text{Y2})$$

where

$$T^*[T_c(\lambda), \lambda] = T_c^0. \quad (\text{Y3})$$

Here, $T_c(\lambda)$ is the shift in the critical temperature due to the appearance of the force λ . T^* has the meaning of a certain modified temperature. $T^*(T, \lambda)$ as well as the "background" function $g(T, \lambda)$ are assumed to be nonsingular functions of their arguments.

Lastly (III) it is supposed that there exists a constraint on the variable a :

$$\langle a \rangle = Y(T, \lambda) \quad (V4)$$

where triangular brackets denote ensemble average. Y is also meant to be a nonsingular function. The critical temperature of the system with the constraint (V4) is a solution of (V3) together with

$$\begin{aligned} \langle a(\vec{r}) \rangle &= \left(\frac{\partial F}{\partial \lambda} \right)_T = \left[\frac{\partial F_0(T^*(T, \lambda))}{\partial \lambda} \right]_T + \left(\frac{\partial g}{\partial \lambda} \right)_T = \\ &= -S_0 [T^*(T, \lambda)] \left(\frac{\partial T^*}{\partial \lambda} \right)_T + \left(\frac{\partial g}{\partial \lambda} \right)_T \end{aligned} \quad (V5)$$

This last expression must be by (V4) equal to $Y(\lambda, T)$, so

$$\left(\frac{\partial g}{\partial \lambda} \right)_T - Y(\lambda, T) = S_0(T^*) \left(\frac{\partial T^*}{\partial \lambda} \right)_T \quad (V6)$$

The assumptions (I), (II), and (III) are necessary for renormalization to occur.

After BE we assume a compressible Ising Hamiltonian H in zero field in the form

$$\begin{aligned} H + \lambda \sum_r \left(\sum_{ij} \right)_{\epsilon r} \xi_{ij} = \\ = \sum_i \frac{p_i^2}{2m} + \sum_{(ij)} [\phi(\xi_{ij}) + J(\xi_{ij}) \sigma_i \sigma_j] + \lambda \sum_r \left(\sum_{ij} \right)_{\epsilon r} \xi_{ij}, \end{aligned} \quad (V7)$$

where $\xi_{ij} = (\vec{r}_{ij} \cdot \vec{R}_{ij}) / |\vec{R}_{ij}|$ connecting nearest neighbors in a d -dimensional cubic lattice of N spins is the projection of the instantaneous vector separation $\vec{r}_{ij}$ into the equilibrium vector

separation $\vec{R}_{ij}$, ϕ denotes lattice part of the Hamiltonian, $\sum_i$ denotes the sum over the rows and λ is the Lagrange multiplier determining the average length of the row.

The following forms were adopted for ϕ and J :

$$\phi(x) = \phi_0 + \frac{1}{2} \phi_2 (x-a_0)^2, \quad (\phi_2 > 0), \quad (V,8)$$

$$J(x) = J_0 + J_1(x-a_0) \quad (V,9)$$

Here, a_0 is the constant and J_0 denotes the exchange integral of a rigid system.

Following GBI we can write down the free energy of the BE model as

$$F(\lambda, T) = -kT \log Z_I \left[\frac{J_{\text{eff}}(\lambda, T)}{kT} \right] - \frac{dNkT}{2} \log(2kT\pi m q_+ q_-), \quad (V,10)$$

where

$$J_{\text{eff}}(\lambda, T) \equiv J_{\text{eff}}(\lambda) = J_0 - \frac{J_1 \lambda}{\phi_2}, \quad (V,11)$$

and

$$\begin{aligned} q_{\pm} &= \int_{-\infty}^{+\infty} d\xi \exp \left\{ -\beta [\phi(\xi) + \lambda \xi \pm J(\xi)] \right\} = \\ &= \exp(-\beta c_{\pm}) (\beta \phi_2 / \pi)^{-1/2}, \quad (\beta = \frac{1}{kT}). \end{aligned} \quad (V,12)$$

$$\begin{aligned} c_{\pm} &= \phi_0 - \frac{1}{2\phi_2} (J_1^2 + \lambda^2) + \lambda a_0 \pm \left(J_0 - \frac{J_1 \lambda}{\phi_2} \right) = \\ &= \phi_0 - \frac{1}{2\phi_2} (J_1^2 + \lambda^2) + \lambda a_0 \pm J_{\text{eff}}(\lambda). \end{aligned} \quad (V,13)$$

Here $Z_I [\beta J_{\text{eff}}(\lambda)]$ denotes the partition function of the rigid Ising model, in which in particular the exchange interaction is a function of λ ; m is the atomic mass.

From Eqs. (V2) and (V10) we see that in this formulation

$$g(T, \lambda) = - \frac{dNkT}{2} \log(2KT\pi m q_+ q_-) =$$

$$= - \frac{dNkT}{2} \left[\log(2KT\pi m) + \log \left(\frac{2kT\pi}{\phi_2} \right) - \frac{1}{kT} \left(2\phi_0 - \frac{J_1^2}{\phi_2} + 2\lambda a_0 - \frac{\lambda^2}{\phi_2} \right) \right] \quad (V14)$$

We confirm that - as it is required - the "background" function $g(T, \lambda)$ is nonsingular, and

$$\frac{\partial g(T, \lambda)}{\partial \lambda} = dN(a_0 - \frac{\lambda}{\phi_2}). \quad (V15)$$

Also, from (V10) we deduce that

$$T^*(T, \lambda) = \frac{TJ_0}{J_{\text{eff}}(\lambda)}. \quad (V16)$$

We note at this point that the formula (V11) for $J_{\text{eff}}(\lambda)$ is valid to all orders in λ . However, as we shall see in the following we will be interested in the case of small λ so upon expanding (V16) we get ($\lambda \ll \phi_2 J_0 / J_1$)

$$T^*(T, \lambda) = T \left(1 + \frac{J_1 \lambda}{J_0 \phi_2} \right) + O(\lambda^2) + \dots \quad (V17)$$

In general, the second order phase transition in a d -dimensional Ising model takes place at a certain value of

$$\frac{J_{\text{eff}}}{kT} = \frac{J_0}{kT} - \frac{J_1 \lambda}{\phi_2 kT} \quad (V18)$$

If the R.H.S. of Eq.(V,18) is equal to C_d - a certain number depending only upon d - then we get explicitly the critical temperature as a function of λ :

$$T_c(\lambda) = \frac{J_0}{C_d k} - \frac{J_1 \lambda}{k \phi_2 C_d} \equiv T_c^0 - \frac{J_1 \lambda}{k \phi_2 C_d} . \quad (V,19)$$

Having substituted now the exact expression (V,19) to (V,17) we get

$$T^* [T_c(\lambda), \lambda] = T_c^0 + O(\lambda^2) + \dots \quad (V,20)$$

Here, T_c^0 is the critical temperature of the ideal system. By Eq.(V,20) the requirement of Eq.(V,3) is seen to be satisfied.

The pressure can be calculated also from Eq. 10) as GBI did

$$P = \frac{\lambda}{[a(\lambda, T)]^{d-1}} \quad (V,21)$$

where

$$a(\lambda, T) = \langle \xi \rangle = \frac{1}{Nd} \frac{\partial F(T, \lambda)}{\partial \lambda} . \quad (V,22)$$

From Eqs.(V,4), (V,21), and (V,22) we conclude that

$$\gamma(\lambda, T) = \left(\frac{\lambda}{P} \right)^{\frac{1}{d-1}} \quad (V,23)$$

which for a given P is a nonsingular function of λ . Therefore, at the constant $P > 0$ the BE model exhibits a second order phase transition with renormalized critical exponents.

3. CALCULATION OF THE CROSSOVER TEMPERATURE

Using the above results and following the recipe of Fisher (see also ref. 58 for related considerations) we shall calculate now the region around $\bar{T}_c$ - the critical temperature in the presence of a constraint within which the renormalization shows up. To this end consider again Eqs. (V6), (V15), and (V17): the solution of Eqs. (V6) and (V17) (where (V15) and (V23) are taken into account) yields the constrained critical point $(\bar{T}_c(P), \bar{\lambda}_c(P))$, see Fig. Eq. (V6) for small λ reads now

$$Nd\left(\frac{\lambda}{P}\right)^{\frac{1}{d-1}} - Nd\left(a_0 - \frac{\lambda}{\phi_2}\right) = -S_0 \left[T^*(T, \lambda)\right] \cdot T \frac{J_1}{J_0 \phi_2} \quad (V24)$$

It can be rewritten at the constrained critical point $(\bar{T}_c, \bar{\lambda}_c)$ with the help of Eqs. (V1) and (V20) as

$$Nd\left(a_c - a_0 + \frac{\bar{\lambda}_c}{\phi_2}\right) = -S_c^0 \bar{T}_c \frac{J_1}{J_0 \phi_2} \quad (V25)$$

This in turn, specified for $P = 0$, using Eq. (V19) transforms into

$$Nd(a_{c,0} - a_0) = -S_c^0 \bar{T}_c \frac{J_1}{J_0 \phi_2} = -S_c^0 \frac{J_1}{C_d k \phi_2} \quad (V26)$$

where $a_{c,0}$ is the value of a at T_c^0 . This might serve as an illustration of the fact that if, for instance, a_0 were taken to be the lattice spacing at $T = 0$, the lattice spacing at T_c^0 differs from a_0 by a term proportional to J_1 . Thus, in our case, a harmonic lattice contracts or expands depending on the sign of spin-lattice coupling J_1 . This is sometimes referred to as an anomalous expansion (48)

Let us now expand the L.H.S. of Eq.(V6) near $(\bar{T}_c, \bar{\lambda}_c)$ to first order in $\Delta\lambda = \lambda - \bar{\lambda}_c$:

$$\begin{aligned} dN \left\{ \left(a_0 - \frac{\bar{\lambda}_c}{\phi_2} \right) - a_c - \left[\frac{1}{\phi_2} - \frac{1}{(d-1)} \left(\frac{1}{P} \right)^{\frac{1}{d-1}} \frac{1}{\bar{\lambda}_c^{\frac{1}{d-1}-1}} \right] \Delta\lambda + \dots \right\} = \\ = dN \left\{ \left(a_0 - \frac{\bar{\lambda}_c}{\phi_2} - a_c \right) \cdot \left[\frac{1}{\phi_2} - \frac{1}{P(d-1)a_c^{d-2}} \right] \Delta\lambda + \dots \right\}, \quad (V,27) \end{aligned}$$

Analogously, we may expand $T^*(T, \lambda) - T^*(\bar{T}_c, \bar{\lambda}_c) = \Delta T^* =$

$T^*(T, \lambda) - T_c^\circ$ in powers of $\Delta\lambda$ and $\Delta\bar{T}$, where

$$\Delta\bar{T} = T - \bar{T}_c, \quad (V,28)$$

$$T^* - T_c^\circ = a_1 \Delta\lambda + a_2 \Delta\bar{T} + \zeta \Delta\lambda \Delta\bar{T} + \dots, \quad (V,29)$$

where

$$a_1 = \frac{\bar{T}_c J_1}{J_0 \phi_2}; \quad a_2 = \left(1 + a_1 \frac{\bar{\lambda}_c}{\bar{T}_c} \right); \quad \zeta = \frac{J_1}{J_0 \phi_2}. \quad (V,30)$$

From Eq.(V,29)

$$\Delta\lambda = \frac{1}{a_1} \Delta T^* - \frac{a_2}{a_1} \Delta\bar{T} + \dots, \text{ and also} \quad (V,31)$$

$$\left(\frac{\partial T^*}{\partial \lambda} \right)_T = a_1 + \zeta \Delta T^* + \dots. \quad (V,32)$$

We remember also that from Eq.(V1)

$$S_0(T^*) = S_c^\circ + A(\Delta T^*)^{1-\alpha} + B \Delta T^* + \dots. \quad (V,33)$$

We use all the above expansions in the constraint equation (6):

$$\begin{aligned} dN \left\{ \left(a_0 - a_c - \frac{P a_c^{d-1}}{\phi_2} \right) - \left[\frac{1}{\phi_2} + \frac{a_c^{2-d}}{P(d-1)} \right] \left(\frac{1}{a_1} \Delta T^* - \frac{a_2}{a_1} \Delta\bar{T} \right) \right\} + \dots = \\ = \left[S_c^\circ + A(\Delta T^*)^{1-\alpha} + B \Delta T^* + \dots \right] (a_1 + \zeta \Delta T^* + \dots), \quad (V,34) \end{aligned}$$

which upon dropping the terms of the order $(\Delta T^*)^{1-\alpha} \cdot \Delta \bar{T}$, $\Delta T^* \Delta \bar{T}$... to the lowest order in P combines to

$$(1 + \kappa'') \Delta \bar{T} = \kappa (\Delta T^*)^{1-\alpha} + (1 + \kappa') \Delta T^*, \quad (V_{35})$$

where

$$\kappa = \frac{P(d-1)a_c^{d-2} A}{Nd} \left(\frac{T_c J_1}{J_0 \phi_2} \right)^2 \cong \frac{P(d-1)a_c^{d-2} A}{Nd} \left(\frac{J_1}{C_d^k \phi_2} \right)^2, \quad (V_{36})$$

$$\kappa' = \kappa \frac{B}{A}, \quad (V_{37})$$

$$\kappa'' = \frac{Pa_c^{d-1}}{\phi_2} \left[\frac{J_1}{J_0 \phi_2} + (d-1)a_c - \left(\frac{J_1}{C_d^k \phi_2} \right)^2 \frac{S_c^0}{Nd} \right]. \quad (V_{38})$$

Our basic equation (V₃₅) in the limit $P \rightarrow 0$ gives $\Delta \bar{T} \sim \Delta T^*$, where the proportionality sign means that no constants depending on P are involved. On the other hand, when P is being kept constant, Eq. (V₃₅) yields a nonalgebraic relation between $\Delta \bar{T}$ and ΔT^* that causes a change of effective exponents, i.e. the renormalization^(54,58). Accordingly, the quantities κ , κ' , κ'' - all proportional to P , measure the deviation from an ideal behavior.

We can consider, after Fisher⁽⁵⁴⁾, the solution of Eq. (V₃₅) for small α . For $\Delta \bar{T} \rightarrow 0$ the dominant term in R.H.S. of (V₃₅) is $\kappa (\Delta T^*)^{1-\alpha}$ so

$$\begin{aligned} \kappa (\Delta T^*)^{1-\alpha} &\cong (1 + \kappa'') \Delta \bar{T}, \quad \text{and} \\ \Delta T^* &\cong \left(\frac{\kappa}{1 + \kappa''} \right)^{\frac{1}{\alpha-1}} (\Delta \bar{T})^{\frac{1}{1-\alpha}}. \end{aligned} \quad (V_{39})$$

Rewrite now Eq. (V₃₅) as

$$(1 + \kappa') \left[1 + \frac{\kappa}{1 + \kappa'} (\Delta T^*)^{-\alpha} \right] \Delta T^* = (1 + \kappa'') \Delta \bar{T} \quad \text{and}$$

for ΔT^* in square brackets substitute Eq. (V39). Then we get

$$\Delta T^* = \left(\frac{1 + \kappa''}{1 + \kappa'} \right) \frac{\Delta \bar{T}}{1 + \frac{\kappa}{1 + \kappa'} \left(\frac{1 + \kappa''}{\kappa} \Delta \bar{T} \right)^{\frac{1}{1-a}}}, \text{ which is}$$

equivalent to

$$\Delta T^* = \left(\frac{1 + \kappa''}{1 + \kappa'} \right) \frac{\Delta \bar{T}^{\frac{1}{1-a}}}{(\Delta \bar{T})^{\frac{a}{1-a}} + (\Delta T_x)^{\frac{a}{1-a}}} \quad (V40)$$

where

$$\begin{aligned} \Delta T_x &= \left(\frac{\kappa}{1 + \kappa'} \right)^{\frac{1-a}{a}} \cdot \left(\frac{\kappa}{1 + \kappa''} \right) \approx \kappa^{\frac{1}{a}} (1 - \kappa'' + \dots) (1 - \kappa^{\frac{a-1}{a}} + \dots) = \\ &= \left[P(d-1) \frac{A(\bar{T}_c J_1)^2}{Nd(J_0 \phi_2)^2} a_c^{d-2} \right]^{\frac{1}{a}} \cdot \left[1 + O(PJ_1^2) + \dots \right] \quad (V41) \end{aligned}$$

It is not difficult to discern some general properties of Eq. (V40). When $\Delta \bar{T}$ is small (i.e. smaller than ΔT_x) then

$\Delta T^* \sim (\Delta \bar{T})^{\frac{1}{1-a}}$ and the renormalization occurs. If $\Delta T \gg \Delta T_x$, then $\Delta T^* \sim \Delta T$ and there is no renormalization. ΔT_x plays the role of the "cross-over" temperature between two regions. Eq. (V41), with the help of Eq. (V19) tells us that to the lowest order in P

$$\Delta T_x \sim (PJ_1^2)^{\frac{1}{a}} \quad (V42)$$

When there is no magnetoelastic coupling, i.e. $J_1 \equiv 0$, there is no renormalization at all: $\Delta T_x = 0$. Eq. (V42) defines a sort of "cone" around $T_c(\lambda)$ having the cusp at T_c^0 (see Fig. 15). In the presence of a constraint the transition is not approached at

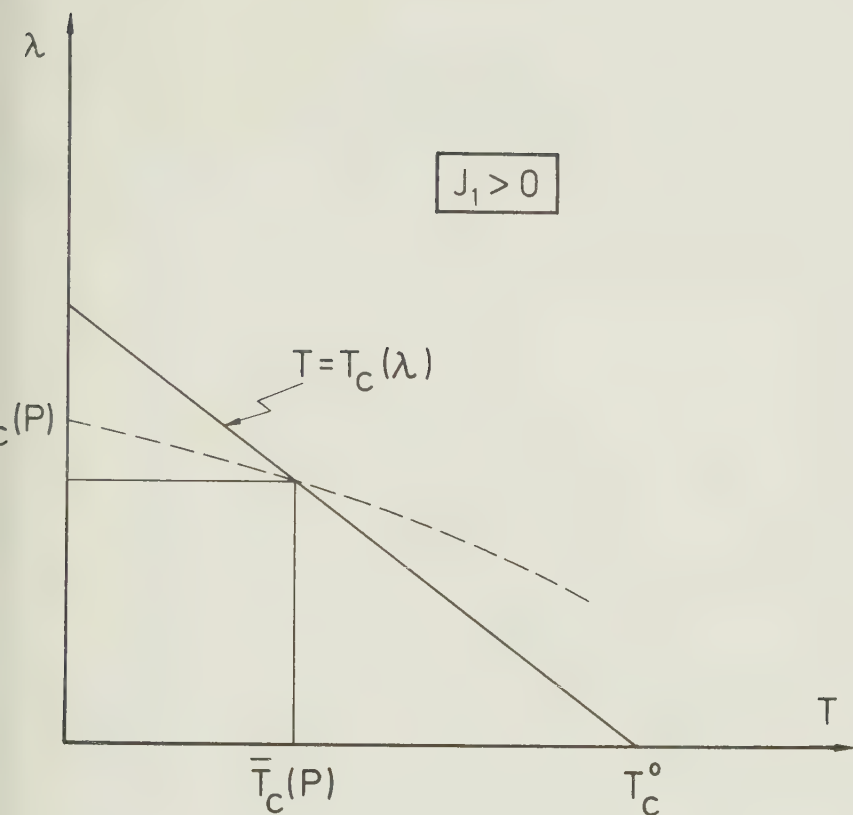


Fig. 15: Solid line represent line of unconstrained critical points. Dashed line is the projection of on (T, λ) plane of the intersection of $a = a(\lambda, T)$ and $a = \gamma(\lambda, T)$. $(\bar{T}_C, \bar{\lambda}_C)$ is the constrained critical point. The system is approaching $\bar{T}_C$ along dashed line.

a constant λ but the system follows a certain path in (T, λ) plane, illustrated by dashed lines for different pressures in Fig. 16. This path is a projection on the (T, λ) plane of the intersection of two surfaces: $a = a(\lambda, T)$ and $a = Y(\lambda, T)$. In turn, the intersection of this line with $T_c(\lambda)$ line gives the constrained critical point $(\bar{T}_c, \bar{\lambda}_c)$. Since for $P \rightarrow 0$, ΔT_x shrinks to zero for $P = 0$, it means that under the constraint $P = 0$ the system behaves ideally. This again agrees with the assumption II of Fisher because $P = 0$ corresponds to $\lambda = \text{const} \equiv 0$.

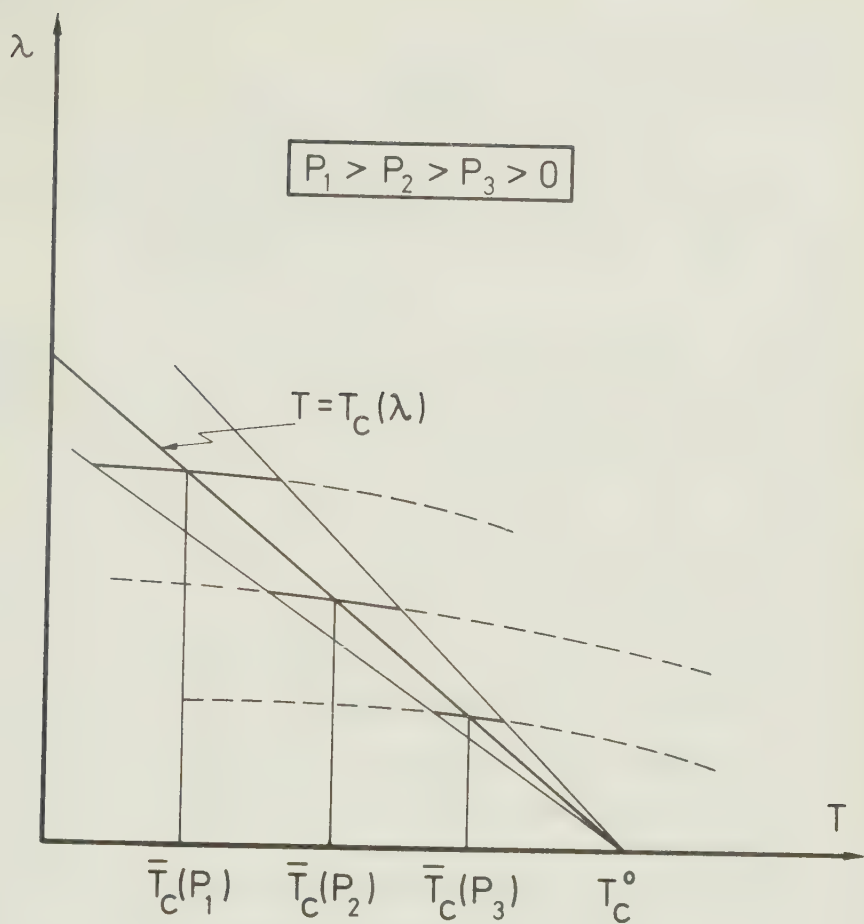


Fig. 16: Several constrained critical points for P close to zero. The region inside the cone around $T_C(\lambda)$ corresponds to renormalized behaviour and is represented by solid parts of dashed lines.

4. CONCLUSIONS AND DISCUSSION

The Statistical Mechanics results on the compressible magnetic Ising model of the Baker-Essam type in d dimensions were shown to comply explicitly with the requirements of Fisher's theory of renormalization of critical exponents.

It is the solubility of the model in the λ -ensemble (Eq. (V,11)) which made it possible to find in a simple way the range of temperature around T_c over which the renormalization is important.

The perspectives of experimental observation of the renormalization of exponents are not very promising owing to the fact that ΔT_x (Eq. (V,41)) is usually very small. They were claims, however, to observe this effect experimentally using the light scattering in ternary mixtures⁽⁵⁹⁾. The ideal system here is a binary mixture. These experimental results support partly the numerical results of decorated Ising models⁽⁶⁰⁾. Guttman⁽²²⁾ has considered the size of the renormalization effect using the original version of the BE model and arrived at the conclusion that in real crystals the effect, if observable at all, should be very small. This fully agrees with our results based on the general theory of systems with "hidden" ⁽⁵⁴⁾ (here lattice) variables.

APPENDIX A

PARTITION FUNCTION FOR THE n-VECTOR MODEL

Consider the model Hamiltonian

$$\begin{aligned} H(n,d) &= - \sum_{\langle ij \rangle} \sum_{\alpha=1}^n J_{ij} S_i^{\alpha} S_j^{\alpha} = \\ &= - \sum_{\langle ij \rangle} J_{ij} \vec{S}_i^{(n)} \cdot \vec{S}_j^{(n)}, \end{aligned} \quad (A,1)$$

where the summation is over the points of a d-dimensional regular lattice and the quantities $S^{(n)}$ are isotropically-interacting n dimensional classical spins of length 1

$$\vec{S}_i = (S_i^1, S_i^2, \dots, S_i^n), \quad (A,2)$$

where

$$\sum_{\alpha=1}^n (S_i^{\alpha})^2 = 1$$

The Hamiltonian (A,1) in its general form was first proposed by Stanley⁽¹⁰⁾ and has come to be called the n-vector model. It reduces for three special cases to three commonly-studied models;

for $n = 1$ it is the simple spin half Ising model;

for $n = 2$ (A,1) describes a system of isotropically interacting 2-d vectors and is called plane rotator model or classical X-Y model;

for $n = 3$ (A,1) describes the classical Heisenberg model.

It has been pointed out ⁽¹⁰⁾ that (A,1) is exactly soluble for $d = 1$ and arbitrary n .

In this case, for N spins in the chain

$$H(n,1) \equiv H^{(n)} = - \sum_l^{N-1} J_l \vec{S}_l^{(n)} \cdot \vec{S}_{l+1}^{(n)} . \quad (A,4)$$

We emphasize that $H(n,1)$ remains soluble for an arbitrary set of coupling constants $\{J_i\}$.

The partition function corresponding to (A,4) is a product of partition functions Z_l of separate bonds J_l ,

$$\begin{aligned} Z_N^{(n)}(\tau, \{J_l\}) &= \text{const.} \prod_{l=1}^{N-1} Z_l = \\ &= (1 + \delta_{1,n}) \cdot \prod_{l=1}^{N-1} \left(\frac{\beta J_l}{2} \right)^{1 - \frac{n}{2}} \Gamma\left(\frac{n}{2}\right) I_{\frac{n}{2}-1}(\beta J_l) , \end{aligned} \quad (A,5)$$

where $\Gamma(x)$ is the gamma function and $I_\nu(x)$ is the modified Bessel function of first kind of the order ν .

It reduces to

$$Z_N^{(1)} = 2^N \prod_{l=1}^{N-1} \cosh(\beta J_l) , \quad \text{for } n = 1 , \quad (A,6)$$

$$Z_N^{(3)} = \prod_{l=1}^{N-1} \frac{\sinh(\beta J_l)}{\beta J_l} \quad \text{for } n = 3 . \quad (A,7)$$

The nearest neighbour spin-spin correlation functions can be calculated from the formula

$$Z_N^{(n)} \langle \vec{S}_l^{(n)} \cdot \vec{S}_{l+1}^{(n)} \rangle = \frac{\partial}{\partial (\beta J_l)} \sum_{\{s\}} \exp\left(\sum_{l'=1}^{N-1} \beta J_{l'} \vec{S}_{l'}^{(n)} \cdot \vec{S}_{l'+1}^{(n)} \right) , \quad (A,8)$$

where $\sum_{\{s\}}$ denotes the sum over the spin configurations.

Using (A,5), the Eq. (A,8) can be calculated to give

$$\langle \vec{S}_l^{(n)} \cdot \vec{S}_{l+1}^{(n)} \rangle = \frac{I_{n/2}(\beta J_l)}{I_{n/2-1}(\beta J_l)} . \quad (A,9)$$

This last expression is equal to $\tanh(\beta J_L)$ and $\coth(\beta J_L) - (\beta J_L)^{-1}$ for $n = 1$ and $n = 3$ respectively.

Although it is difficult to envisage the spins having $n > 3$ dimensions, it has been recently shown that $n > 3$ vector models still continue to describe certain real physical systems (65).

APPENDIX B

LANDAU THEORY AND FIRST ORDER PHASE TRANSITIONS

The Landau theory of phase transitions is based on the assumption that the free energy can be expanded in Taylor series in terms of the (small) order parameter ,

$$F = F(\eta, T) = F_0 + a\eta^2 + b\eta^4 + c\eta^6 + \dots, \quad (B,1)$$

where a, b and c are functions of the temperature and parameters of the system. Since the equilibrium values of the order parameter are determined by the minima of $F: \frac{\partial F}{\partial \eta} = 0$, the existence and the order of phase transitions depend on the character of minima of (B,1). If (B,1) has no more than one minimum then the transition is of second order. This is usually achieved by assuming

$$a(T) = a'(T - T_c), \quad b(T_c) > 0, \quad c(T_c) > 0. \quad (B,2)$$

For $T > T_c$ $\eta = 0$ is the only minimum. For $T < T_c$, we can neglect the sixth order term and the minimum

$$\eta(T) = \left[\frac{a'}{2b} (T_c - T) \right]^{1/2} \quad (B,3)$$

goes smoothly to zero at $T=T_c$, indicating the second order phase transition at $T=T_c$.

If the condition $b(T_c) > 0$ is disposed of, then for some values of T for which $b < 0$, $c > 0$ a second minimum of the free energy at $\eta \neq 0$ in addition to that at $\eta = 0$ can appear.

The second order transition line ends then at the point $a=0, b=0$ and merges into first order transition line. This last line is defined by the condition that the two minima: at $\eta=0$ and at $\eta \neq 0$ become equal. In other words

$$F(\eta) = F_c \quad (B,4a)$$

$$\frac{\partial F}{\partial \eta} = 0 \quad (B,4b)$$

define the first order transition line.

If $b(T)$ changes its sign for a certain temperature T_0 , i.e.

$b(T) = b' \cdot (T - T_0)$, $c > 0$ one can show that the critical exponents take on different values, depending on the distance from the point T_t defined as the solution of $a=b=0$ or, equivalently

$$T = T_c(p_i) \quad (B,5a)$$

$$T = T_0(p_i) \quad , \quad (B,5b)$$

where p_i denote the parameters of the system.

The values of critical exponents near T_t can be simply obtained from (B,1) as was done in (25). They were quoted in Chapter II.

APPENDIX C.

THE JORDAN-WIGNER TRANSFORMATION

The Jordan-Wigner transformation⁽⁶³⁾ relates the set of Pauli operators a_l which satisfy a "mixed" set of commutation rules

$$\{a_l, a_l^\dagger\} = 1, (a_l^\dagger)^2 = (a_l)^2 = 0, [a_l, a_{l'}] = 0, l \neq l' \quad (C,1)$$

to the set of Fermi operators c_l , defined as follows

$$c_l = \exp\left(\pi i \sum_{l'=1}^{l-1} a_{l'}^\dagger a_{l'}\right) a_l, \quad c_l^\dagger = a_l^\dagger \exp\left(-\pi i \sum_{l'=1}^{l-1} a_{l'}^\dagger a_{l'}\right). \quad (C,2)$$

One can show that for $i \neq j$

$$\{c_i, c_j^\dagger\} = 0 \quad (C,3)$$

One proves (C,3) by a direct substitution and by using a general formula valid for Pauli operators

$$e^{x a^\dagger a} f(a, a^\dagger) e^{-x a^\dagger a} = f(a e^{-x}, a^\dagger e^x) \quad (C,4)$$

where x is a C-number and where $f(x, y)$ is an arbitrary analytical function of its arguments. From (C,4) it follows that

$$a e^{-\pi i a^{\dagger} a} = (-1) e^{-\pi i a^{\dagger} a} a, \quad (C,5)$$

which is necessary to prove (C,3).

Similarly, one can easily show that

$$c_l^{\dagger} c_l = a_l^{\dagger} a_l \quad (C,6)$$

and

$$c_l^{\dagger} c_{l+1} = a_l^{\dagger} a_{l+1} \quad (C,7)$$

With the above relations one sees that the Hamiltonian H_{X-Y} (Eq. (III,11)) has the same structure in terms of a-operators as H_{X-Y} (Eq. (III,13)) in terms of c-operators.

APPENDIX D

CRITICAL TEMPERATURE OF THE DISPLACIVE ANTIFERROELECTRIC WITH AN ARBITRARY V_4

According to Eq. (IV,11) the free energy associated with the antiferroelectric distortion δ is equal

$$f(\delta, T) = \frac{J}{2} \delta^2 - \frac{1}{\beta} \ln \int_{-\infty}^{\infty} d\eta \exp \left[-\beta \left(\frac{V_2}{2} \eta^2 + \frac{V_4}{4} \eta^4 - J \eta \delta \right) \right] \quad (D,1)$$

where the subscript T of J was dropped for simplicity. The critical temperature T_c below which the order parameter δ non-vanishing is obtained from the condition

$$\left. \frac{\partial f}{\partial \delta} \right|_{\delta=0} = 0, \text{ which for (D,1) becomes}$$

$$\frac{1}{\beta_c J} = \frac{\int_{-\infty}^{\infty} d\eta \eta^2 \exp \left[-\beta_c \left(\frac{V_2}{2} \eta^2 + \frac{V_4}{4} \eta^4 \right) \right]}{\int_{-\infty}^{\infty} d\eta \exp \left[-\beta_c \left(\frac{V_2}{2} \eta^2 + \frac{V_4}{4} \eta^4 \right) \right]}, \quad (D,2)$$

where the property $f(\delta, T) = f(-\delta, T)$ was used. By introducing now a new variable $y = \left(\frac{\beta V_4}{4} \right)^{1/4} \eta$ the Eq. (D,2) can be rewritten as

$$\frac{1}{J} = \frac{2}{(\beta_c V_4)^{1/2}} \frac{\int_{-\infty}^{\infty} dy y^2 \exp \left[-\left(\frac{\beta_c V_2^2}{4} \right)^{1/2} y^2 - y^4 \right]}{\int_{-\infty}^{\infty} dy \exp \left[-\left(\frac{\beta_c V_2^2}{4} \right)^{1/2} y^2 - y^4 \right]}. \quad (D,3)$$

We are going to show now that the Eq. (D,3) can be expressed in terms of known functions. To this end we observe that the integrals appearing in (D,3) can be related to the integral representation of the parabolic cylinder function $D_\nu(z)$ of the order ν (40):

$$D_\nu(z) = \frac{e^{-\frac{1}{4}z^2}}{\Gamma(-\nu)} \int_0^\infty dt e^{-zt - \frac{1}{2}t^2} t^{-\nu-1}. \quad (D,4)$$

By two consecutive changes of variables $t = y^2$ and $y = 2^{\frac{1}{4}}x$ (D,4) can be rewritten in the equivalent form (with $\nu = -\frac{1}{2}$) as

$$2^{\frac{1}{4}} \Gamma(\frac{1}{2}) e^{\frac{1}{4}z^2} D_{-\frac{1}{2}}(z) = \int_{-\infty}^{\infty} dx e^{-\sqrt{2}zx^2 - x^4}. \quad (D,5)$$

We quote also the expression for the derivatives of parabolic cylinder functions (40):

$$\frac{d}{dz} [e^{\frac{1}{4}z^2} D_\nu(z)] = (-1)(-\nu) e^{\frac{1}{4}z^2} D_{\nu-1}(z). \quad (D,6)$$

Using now Eqs. (D,5) and (D,6) the implicit equation for T_c (Eq. (D,3)) takes on the final form

$$\left(\frac{1}{\beta_c}\right)^{\frac{1}{2}} \left(\frac{V_4}{32J^2}\right)^{\frac{1}{2}} = \frac{D_{-\frac{1}{2}}\left[\left(\frac{\beta_c V_2}{2V_4}\right)^{\frac{1}{2}}\right]}{D_{-\frac{3}{2}}\left[\left(\frac{\beta_c V_2}{2V_4}\right)^{\frac{1}{2}}\right]} \quad (D,7)$$

which is, of course, valid for all the values of the para-

meters involved. In particular, (D,7) describes T_c as a function of arbitrary V_4 , thereby generalizing the approximate treatment for small V_4 of Chapter IV. The Eq. (D,7) describes also the critical temperature for ferroelectric distortion if the quantity J were interpreted as J_0 rather than $J\pi$.

SUMMARY

We have carried out a theoretical study of several mechanisms leading to the structural Peierls lattice transition in one-dimensional systems. In addition to the electron-lattice interaction which gives rise to the conventional Peierls transition⁽⁸⁾, we have investigated the Peierls transition due to the spin-lattice interaction. Exactly soluble one-dimensional spin models: classical isotropic n -vector model and quantum-mechanical anisotropic $S = \frac{1}{2}$ X-Y models coupled to a single mode of the harmonic lattice were used to analyse the spin-lattice interaction driven lattice transition (spin-Peierls transition). Spin-Peierls transition was found to be of first or second order for classical spin systems and of second order only for quantum systems. The character of the spin-Peierls transition was found to depend crucially on the lattice independent part of the exchange interaction J_0 . By increasing J_0 , which is the measure of spin correlations, the transition temperature of the lattice distortion decreases, the order of transition may change (in classical case) and the $T = 0$ lattice distortion may vanish (classical) or will be reduced (quantum case). We have found that the appearance of the lattice distortion can produce a so-called spin-dimerized state (classical spins, Fig. 3b,c)

In order to study anharmonicity effects on the Peierls transition, we have considered also a ferroelectric Hamiltonian of the displacive type in addition to the linear in lattice variables electron-lattice interaction. These two mechanisms were observed to be cooperative in producing the lattice distortion. We have also developed a formalism allowing for the study of the combined antiferroelectric (Peierls type) and uniform ferroelectric lattice distortion from the ferroelectric lattice Hamiltonian only.

Finally, the critical magnetic behavior of the $d > 1$ magnetic system coupled to the lattice was analysed using exactly soluble magneto-elastic Baker-Essam model. Its exact solubility derives from the one-dimensional character of lattice variables, in close analogy to model systems used to investigate the spin-Peierls transition. The magnetic critical exponents were shown to take on new "renormalized" values in a certain new critical region near T_c . The size of this critical region was calculated as a function of pressure using Fisher's theory of critical behavior in coupled systems.

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